Disertation presented to receive the degree Doctor of
the Rovira I Virgili University
European PhD

Soybean Oil Based Copolymers Containing Silicon, Boron or Phosphorus: Polymerization, Characterization and Fire Retardance Properties

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Tarrgona Enero 2010

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CERTIFICAMOS:

Que el presente trabajo, titulado "Soybean oil Based Copolymers Containing Silicon, Boron or Phosphorus: Polymerization, Characterization and Fire Retardance Properties" presentada por Marta Sacristán Benito para la obtención del título de Doctor, ha sido realizado bajo nuestra dirección en el Departamento de Química Analítica y Química Orgànica de esta Universidad y que cumple los requisitos para poder optar a la Mención Europea.

Tarragona, 7 de enero de 2010

Dra. Marina Galià Clua   Dr. Joan Carles Ronda Bargalló

Al término de esta etapa de mi vida, quisiera dar las gracias a la Dra. Virginia Cádiz por darme la oportunidad de realizar esta tesis en su grupo y especialmente a mis directores, la Dra. Marina Galià y el Dr. Joan Carles Ronda por su ayuda y dedicación durante estos años.

A todos los profesores del área, por estar siempre dispuestos a ayudar.

I would like to thank Professor Dr. Richard Hull, from the University of Lacashire, not only for accepting me in his group, but also for his scientific advice and encouragement. I would also like to thank Dr Anna Stec for her helpful advices. My thanks to Artur, Jenny, Parina, Cameron, David and Tamar for their help and friendship.

A todos los compañeros de laboratorio, gracias por los buenos momentos que hemos vivido juntos y por prestarme vuestra ayuda siempre que la he necesitado. A los que ya se fueron (Gerard, Omar, Robert, David y Patri). A las chicas del 330, Mireia, Silvana y Mercé por las conversaciones mantenidas y el chocolate compartido. A Vanessa. A Quique y David por transmitirme su afición a la "psicología". A los nuevos Cristina, Maryluz y Camilo que me han hecho sonreir durante los últimos meses. A Marisa por compartir tantos momentos conmigo. A Lucas, por su apoyo, ayuda y sobre todo su amistad; sin el cual, estos años hubiesen sido muy distintos.

A mis padres, gracias por animarme a seguir siempre adelante y apoyarme incondicionalmente en todas las decisiones de mi vida. A mi hermana cómplice y amiga.
A Ángel por su cariño, apoyo y comprensión, y por todos esos momentos que nos hemos perdido por esta Tesis.

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1. Introduction and Scope

1.1 Sustainable development

The sustainable development concept came out of the United Nations Commision on Environment and Development in 1987 (Bruntland Commission)[1] and it is defined as "the development that meets the needs of the present without compromising the ability of future generations to meet their own needs". Although the ideals on which sustainable development is based were not new, indeed Thomas Jefferson made similar comments in 1789, the Bruntland Commission did catalyse the sustainability debate. From this point, both the society and the industry have considered what a sustainable development really means and the best ways to start to achieve it from their own standpoints.

The principles of the United Nations Conference on environment and Development (UNCED) held in June 1992 in Rio de Janeiro, and Agenda 21,[2] were formulated with the aim of preparing the world for the challenges of the 21st century. The conservation and management of resources for the development were the main focuses of interest, to which the sciences had to make a considerable contribution. Natural, economic and social sciences had to be integrated in order to achieve this aim.

In this context, during the early 1990s the US Environmental Protection Agency (EPA) coined the phrase Green Chemistry "To promote innovative chemical technologies that reduce or eliminate the use of generation of hazardous substances in the design, manufacture and use of chemical products". Over the last 10 years, Green Chemistry has gradually become recognized as both a culture and methodoly for achieving sustainability. The 12 principles of Green Chemistry (they are presented further below) help to

show how this can be achieved.[3]

1. It is better to prevent waste than to treat or clean up waste after it has been created.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. 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. Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. 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. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. 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. 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. 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 main challenges of Green Chemistry and Engineeiring 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, re-using products, recovering and recycling materials. So making processes globally more efficient.

Because of base chemicals are produced in large quantities, their resource-saving production is especially important for sustainable development. These base chemicals affect directly the chemical products, which need to be designed in such a way that they can be processed in a sustainable way.

To avoid the disscusion about the contribution of chemistry to sustainable development a precise definition of the term of "sustainability" was proposed in 2002 in Johannesburg.[4] In ages of depleting fossil oil resserves and an increasing emission of green house gases it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development. In particular, this can provide a constant raw material basis for daily life products and avoid further contribution to green house effects due to CO_2 emission minimization. Furthermore, the utilization of renewable raw materials, taking advantage of the synthetic potential of nature, can (in some cases) meet other principles of green chemistry, such as a built-in design for degradation or an expected lower toxicity of the resulting products.[5]

1.2. Using renewable resources: polymers based in vegetable oils

At present, the feedstocks of the chemical industry are predominantly depleting fossil feedstocks and only a small percentage are renewable (aproximately 12%).[6] Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars, wood, and others.[5]

Now, in the 21st century, polymer materials are used in many different areas in everyday life. Most of the current polymers are produced from fossil sources. Because of their broad use, polymers make a significant contribution to the increasing amount of solid waste. Moreover, efforts such as recycling and combustion in incineratig plants have to be considered carefully from economic and ecological perspectives.

For these reasons, nowadays, there is a growing effort to produce polymers based in vegetable oils. These polymers have some advantages compared with polymers from petroleum-based monomers, because some of them are cheaper and biodegradable. The life cycle of vegetable-oil-based polymers is shown in Figure 1.
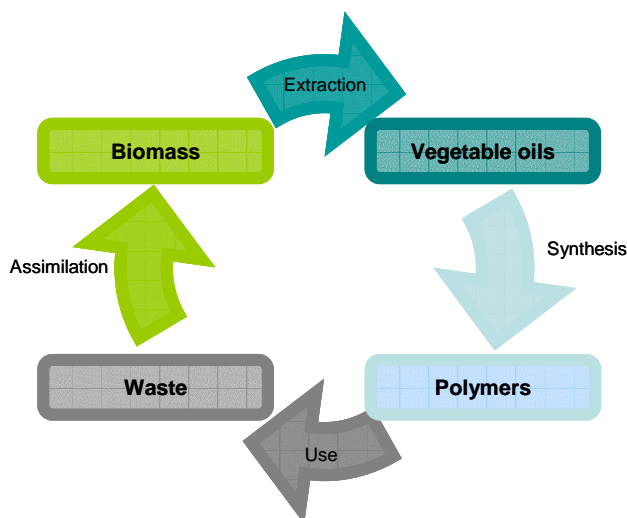
Figure 1. Life cycle of polymers based on vegetable oils.

Composition and reactivity of vegetable oils

Vegetable oils are triglycerides (tri-esters of glycerol with long-chain fatty acids, Figure 2) with varying composition of fatty acids depending on the plant they are extracted from. Triglycerides contain fatty acids with a varying number of carbons (from 10 to 24) and are liquid at room temperature. The most important parameters affecting the physical and chemical properties of such oils are the stereochemistry of the double bonds of the fatty acid chains, their degree of unsaturation as well as the length of the carbon chain of the fatty acids. The degree of unsaturation, which can be expressed by the iodine value (amount of iodine in g that can react with double bonds present in 100 g of sample under specified conditions), can be used as a simple parameter to divide oils into three classes: drying, semi-drying and non-drying oils. Table 1 summarizes the

chemical composition of some industrially important vegetable oils.
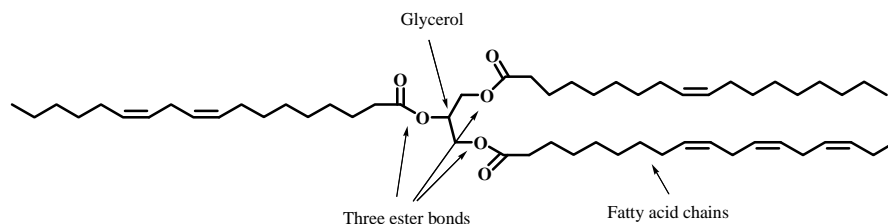
Figure 2. General structure of triglycerides.

There is a big number of fatty acids, the most common are presented in Figure 3.
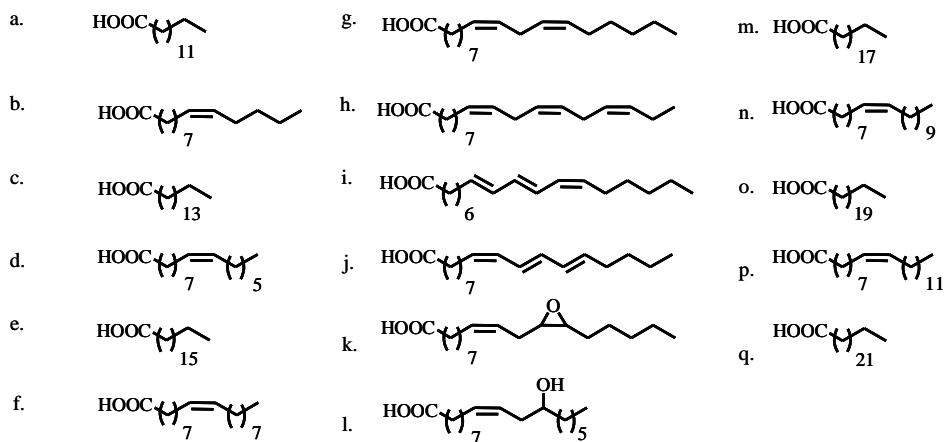
Figure 3. Structure of some common fatty acids. Mistiric (a), mirystoleic (b), palmitic (c), palmitoleic (d), stearic (e), oleic (f), linoleic (g), linolenic (h), calendic (i), α-eleostearic (j), vernolic (k), ricinoleic (l), arachidonic (m), gadoleic (n), behenic (o), erucic (p), lignoceric (q).

Table 1. Composition of different vegetable oils.

Fatty acid	C:DB[a]	Canola	Corn	Cotton seed	Linseed	Olive	Palm	Rapeseed	Soybean	High Oleic[b]
Mistiric	14:0	0.1	0.1	0.7	0.0	0.0	1.0	0.1	0.1	0.0
Myristoleic	14:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Palmitic	16:0	4.1	10.9	21.6	5.5	13.7	44.4	3.0	11.0	6.4
Palmitoleic	16:1	0.3	0.2	0.6	0.0	1.2	0.2	0.2	0.1	0.1
Margaric	17:0	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0
Margaroleic	17:1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Stearic	18:0	1.8	2.0	2.6	3.5	2.5	4.1	1.0	4.0	3.1
Oleic	18:1	60.9	25.4	18.6	19.1	71.1	39.3	12.2	23.4	82.6
Linoleic	18:2	21.0	59.6	54.4	15.3	10.0	10.0	13.2	53.2	2.3
Linolenic	18:3	8.8	1.2	0.7	56.6	0.6	0.4	9.0	7.8	3.7
Arachidonic	20:0	0.7	0.4	0.3	0.0	0.9	0.3	0.5	0.3	0.2
Gadoleic	20:1	1.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	0.4
Eicosadienoic	20:2	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0
Behenic	22:1	0.3	0.1	0.2	0.0	0.0	0.1	0.5	0.1	0.3
Erucic	22:1	0.7	0.0	0.0	0.0	0.0	0.0	49.2	0.0	0.1
Lignoceric	24:0	0.2	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0
DB/Triglyceride		3.9	4.5	3.9	6.6	2.8	1.8	3.8	4.6	3.0

[a] C, number of atom carbons. DB, number of double bonds.

[b] Genetically engineered high oleic acid content soybean oil (Dupont).

Triglycerides have different reactive points that can act as active sites in different reactions: ester groups, double bonds, allylic positions and α-position of ester groups. For this reason, it is expected that triglycerides play a key role during the 21st century to synthesize polymers from renewable sources.[7]

Chemical modification and polymerization of vegetable oils

Through the chemical modification of triglycerides a large number of polymerizable monomers can be obtained. In this way, it is possible to obtain linear,[6] hyperbranched[8] or cross-linked structures.[6,7]

The epoxidation of the double bonds is the most important functionalization reaction and it can be done with hydrogen peroxide[9] or by enzimatic oxidation.[10]

Moreover the epoxidation reaction makes triglycerides capable of reacting via ring-opening obtaining a wide number of products.[11]

Soybean oil and sunflower oils have been bromoacrylated in the presence of acrylic acid and N-bromosuccinimide. The resulting polymers showed good flame retardant properties due to the presence of bromine in the structure.[12,13]

Other recent examples of fatty acid and vegetable oil-based polymers include the synthesis of polyols through Pd catalyzed cyclotrimerization of fatty acid derivatives for polyurethane synthesis;[14] the synthesis of isocyanate-containing triglycerides;[15] the preparation of thermosets from high oleic sunflower oil,[16,17] and from soybean oil and *p*-dinitrosobenzene *via* an *ene* reaction;[18] the development of a linseed oil-based thermoset *via* ROMP;[19] the cationic polymerization of soybean oil in supercritical CO_2;[20] the synthesis of acrylate and phosphine oxide-containing thermosets[21] and the synthesis of phosphorus-containing polyesters via ADMET.[22]

Direct polymerization of vegetable oils

Triglyceride molecules contain double bonds capable of being polymerized through a free radical or a cationic mechanism.[23] The free-radical polymerization of triglyceride double bonds has received little attention due to the presence of chain-transfer processes to the many allylic positions in the molecule; however, vegetable oils such as linseed and tung oils have been classically exploited as drying oils. The drying power of these oils is directly related to their highly unsaturated nature, which allows them to react with atmospheric oxygen that leads to the formation of a network. These oils are used mostly in paints and coatings, but also in inks and resins.

Cationic polymerization has been widely studied by Larock's group,[24] who have focused on the direct cationic polymerization of the C=C double bonds of natural oils. They have reported the preparation of thermosetting polymers ranging from rubbers to hard plastics by the cationic polymerization of a variety of oils: soybean oil,[25-27] corn,[28] fish,[29,30] tung,[31] and with petroleum-based comonomers such as styrene, divinylbenzene, and dicyclopentadiene in the presence of boron trifluoride diethyl etherate (BFE) as the initiator. The resulting thermosetting materials possess thermal and mechanical properties comparable to those of industrial plastics, as well as some other useful properties, including high damping and shape memory.

The soybean oil is one of the most studied oils and a wide number of rubbers, adhesives and plastic materials and elastomers can be obtained

by cationic polymerization of the regular, low saturated and conjugated soybean oil (their specifications are showed in Table 2). The comonomers more used are styrene and divinylbencene.

Table 2. Composition of different soybean oils.

Soybean oil	C=C		Fatty Acids				
	Conjugated	Number[a]	C16:0[b]	C18:0[b]	C18:1[b]	C18:2[b]	C18:3[b]
Soybean oil	No	4.5	10.5	3.2	22.3	54.4	8.3
Low saturated soybean oil	No	5.1	5.0	3.0	20.0	64.0	9.0
Conjugated low saturated Soybean oil	Yes	5.1	5.0	3.0	20.0	64.4	9.0

[a] The average number of carbon–carbon double bonds calculated by ^{1}H NMR spectral analysis.
[b] For example, C18:2 represents the fatty acid (ester) that possesses 18 carbons and 2 C=C bonds.

Figure 4 shows the representative structure of the cationic polymerization of a triglyceride with styrene and divinylbenzene using boron trifluoride as catalyst.[32] The cationic copolymerization of soybean oil, results in polymers ranging from soft rubbers to hard thermosets, depending on the oil and stoichiometry employed.[26] Their glass transition temperatures are around 60–80ºC.[25] It is published that heterogeneous reactions are produced by mixing the iniciator (BF_3OEt_2) with the soybean oil. This problem was solved using $BF_3.OEt_2$ modified with Norway fish oil ethyl ester as initiator.[25]
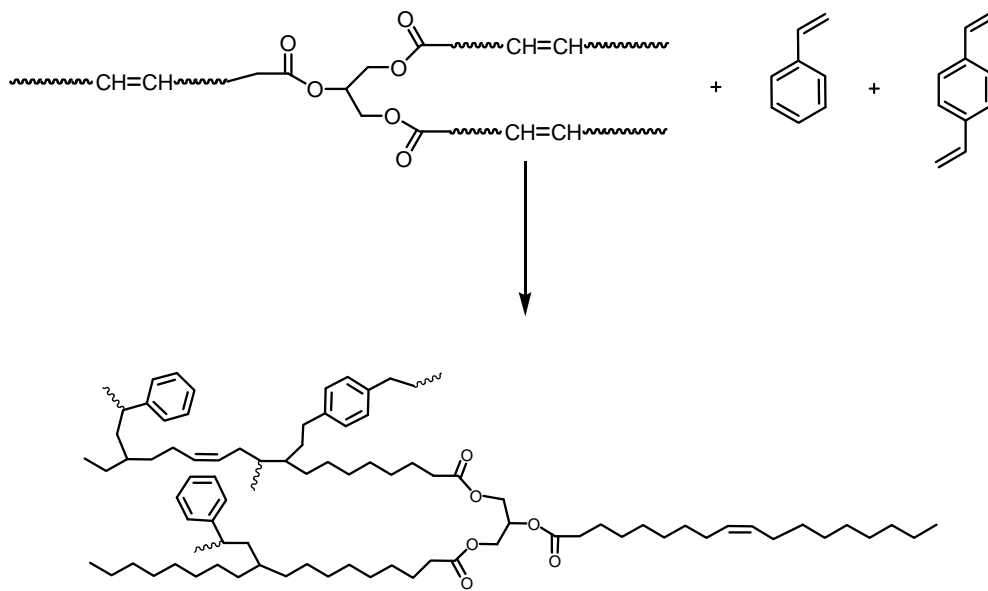
Figure 4. Typical network of soybean oil-styrene-divinylbenzene copolymers.

The BFE-initiated cationic polymerization of simple alkenes is well understood.[33-35] The initiation and propagation mechanisms are shown in Scheme 1. The initiation process occurs in two steps. The BFE first reacts with a small amount of water that may be present in the reaction mixture to produce the hydrate complex. The boron trifluoride hydrate then reacts with the alkene to produce the initiator–coinitiator complex. Propagation may occur through subsequent insertions of the alkene monomer into the initiator–coinitiator complex. Termination may occur at any time during the polymerization through chain transfer to a monomer, chain transfer to a polymer, or through spontaneous termination involving the donation of a proton from the propagating ion pair to the counterion regenerating the boron trifluoride hydrate and producing a double bond in the polymer.

Initiation:

$$BF_3OEt_2 \quad + \quad H_2O \quad \rightleftharpoons \quad BF_3OH_2 \quad + \quad Et_2O$$
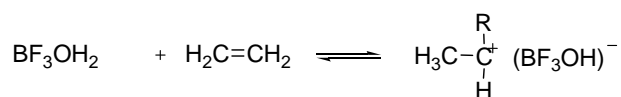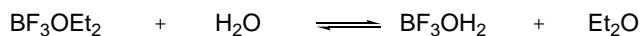
Propagation:
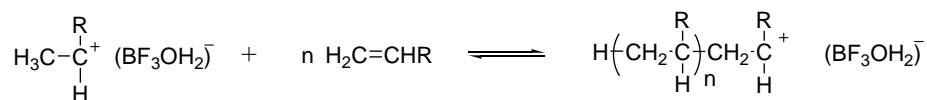
Termination:
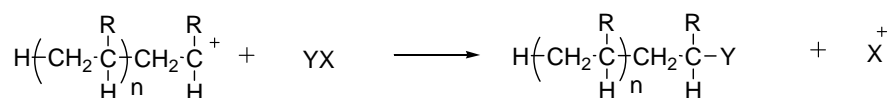
Scheme 1. The mechanism of cationic polymerization of simple alkenes.

The BFE-initiated homopolymerization or copolymerization of triglycerides with alkene comonomers is assumed to follow a similar cationic mechanism. The initiation processes may be similar to those mentioned above. However, the polyunsaturation of the some triglycerides, plus the presence of several different alkene comonomers in these reactions, may complicate the chain propagation mechanisms. The homopolymerization of the triglyceride occurs by repetitive attack by an

electrophilic carbocation on the π systems of the fatty acid ester molecules. The simple homopolymerization of the triglyceride results in only low molecular weight viscous oils in most cases. The introduction of small alkene comonomers not only increases the nucleophilicity of the reactants, but also reduces the steric hindrance. The curing of the thermosets through a cationic mechanism may involve several steps. Copolymerization is also initiated by BFE by the formation and linear growth of chains that soon begin to branch and then crosslink. As the reaction proceeds, the increase in molecular weight accelerates, and eventually several chains become linked together into a network of infinite molecular weight, which corresponds to the gel point, an irreversible transformation from a viscous liquid to an elastic gel or rubber. The polymers lose their ability to flow and are not readily processable beyond this point. Gelation does not necessarily inhibit the curing process. In other words, the reaction rate may remain almost unchanged after the gel point. Vitrification of the growing networks follows when the continuously increasing glass-transition temperature (Tg) of the growing network becomes coincidental with the cure temperature. In the glassy state there is usually a significant decrease in the reaction rate as the reaction becomes diffusion controlled. In order to obtain fully cured networks, the materials are subsequently postcured.

1.3 Safer polymeric materials: fire retardance

As commented before final products should be designed to preserve efficacy of function while reducing risk and toxicity to human health and environment. No mater how clean the production process, however, there remains the question of what happens to a product when it is used in the way it is intended.

During the last few decades the replacement of conventional materials with synthetic polymeric materials has increased dramatically owing to the versatility, low density and sometimes novel properties of the latters. Although synthetic polymers have become widely accepted in almost every application imaginable, most of them are easily fired in presence of a heat source and oxygen.[36] Polymers are a large and growing fraction of the fire load in homes, commercial environments and transportation. The flammability and the resulting destruction of property are not the only problem. Fire fatalities are essentially due to the evolved smoke and toxic gases; in fact, the most common cause of death in fire is smoke and gas inhalation, accounting for over half of fire deaths. This has led to the introduction of stricter legislation and safety standards concerning flammability, and extensive research into the area of flame retardants for polymers has been the result.

The use of fire retardants to reduce combustibility of the polymers, and smoke or toxic fume production, therefore becomes a pivotal part of the development and application of new materials. Amongst the major markets where flame retardants are required, the industries dealing with

construction, electrical and electronics components and transportation are the three of greatest importance.[37]

Until now, many different flame retardants effective in a wide range of polymers have been developed. Most industrial flame retardants are inorganic compounds such as aluminium hydroxide, antimony oxide, zinc borate or ammonium polyphosphates that are added as filers to the polymeric substrate. There are also many different organic flame retardants such as polybrominated, polychlorinated, phosphorous-based and melamine-based compounds, but the marked is dominated by halogenated flame retardants that are mainly used as additives.

Mechanism of polymer flame retardance

In order to understand how flame retardants work, it is first necessary to understand the thermal decomposition processes of polymers. The combustion of a polymeric material is a highly complex process involving a series of different stages ocurring in the condensed phase, gas phase and at the interface between them. The most important step is the fuel production stage, in which an external heat source causes an increase of temperature, resulting in the dissociation of chemical bonds and the evolution of volatile fragments. These fragments diffuse into the surrounding air to create a flammable mixture and combustion is iniciated when this mixture reaches the ignition temperature. Flaming combustion proceeds if the exothermic gas phase combustion reactions generate

sufficient energy, in the form of heat transferred back to the condensed phase, to decompose the polymer further thus producing more fuel and so maintaining the combustion cycle (Figure 5).[38]
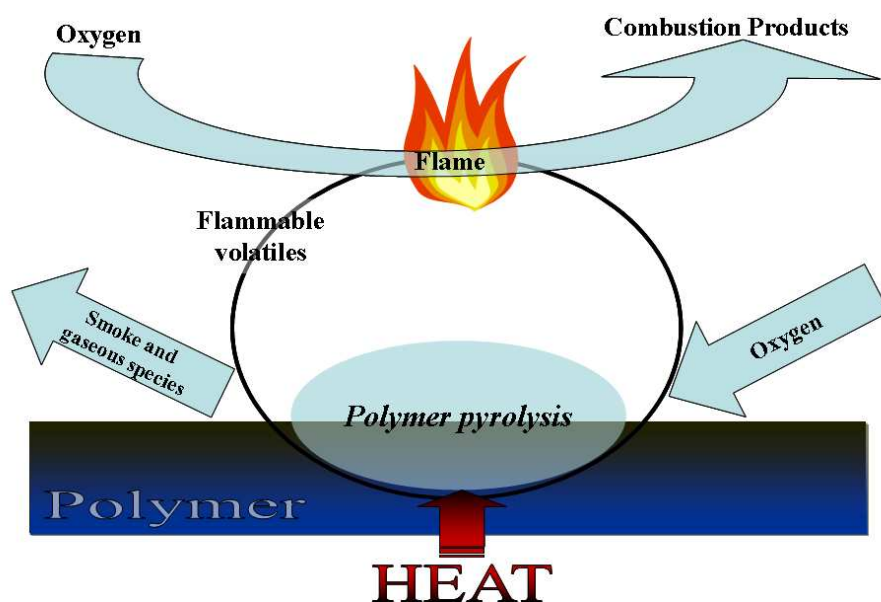
Figure 5. Combustion cycle of polymeric materials.

Successful strategies to reduce the flammability of a material involve breaking into this complex process at one or more stages to reduce the rate and/or change the mechanism.[39] Flame retardants can act by chemical or by physical action and can perform their activity in the condensed phase, in the gas phase or in both depending on their composition.[40]

Physical action: There are several ways in which the combustion process can be retarded by physical action:

- **By cooling.** Endothermic reactions cool the material.

- **By isolation.** The formation of a protective char layer isolates the polymer from heat, oxygen and flames and prevents the volatile products being transported to the polymer surface. One recent innovation consist in ntroducing barrier materials by dispersion of tiny clay particles (with at least one dimension ~ 10 x 10^{-9} m) throughout the polymer that prevents decomposition products being transported to the polymer surface in addition to improve their mechanical properties.

- **By dilution**. The release of inert gases may dilute the volatile flammable compounds.

Chemical action: The chemical activity of flame retardants is based on its interference in the reactions that maintain the combustion in the gas phase or in the reactions involved in the thermal degradation of the polymer in the condensed phase.

- **In the gas phase:** in this case fire retardants act as scavengers of the highly reactive radical species that propagate the combustion.

  For typical hydrocarbon-based polymer fuels the combustion process can be modelled as a set of four radical reactions that involve the initiation, branching, propagation and termination. These radical reactions in the flame can be interrupted by a flame retardant making the radical concentration to fall below a critical value, and the flame goes out. The processes releasing heat are thus stopped, and the system cools down. This is the mode of

action for halogenated flame retardants, the longest established group of fire retardants.

First the flame retardant breaks down to different radicals, [1] which react to form the hydrogen halide [2] that interferes with the radical chain mechanism successively:

[1] $RX = R\cdot + X\cdot$

[2] $X\cdot + RH = R\cdot + HX$

[3] $HX + \cdot OH = H_2O + X\cdot$

[4] $HX + H\cdot = H_2 + X\cdot$
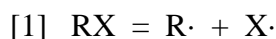
The actual flame retardant effect is thus produced by HX. Previously the decisive stage of inhibition was believed to take place according to Eq. [3], but more recent studies suggest the reaction according to Eq. [4] to be responsible.

Recent environmental pressures have driven market demands to replace halogen based flame retardants with halogen free fire retardants, and this has been the main driver in recent fire retardancy research. In addition, interfering with the flame reactions often results in highly toxic, corrosive and irritant products, including hydrogen halides, dioxins and halobenzofurans, generally increasing the toxicity of the fire gases while reducing fire growth.

• **In the condensed-phase:** in this case fire retardants interfere the thermal degradation processes modifying the reaction pathways and promoting the formation of char instead of volatile degradation products.

The flame retardant or its thermal decomposition products catalyzes dehydration and condensation reactions that lead to cross-linking. These processes contribute to formation of a char layer over the polymer surface. This solid residue isolates the non-burned surface from heat, oxygen and flames and prevents the volatile products being transported to the polymer surface.

Different fire retardants act in different ways, but all need to be matched to their host polymer. Moreover, some flame retardants are effective by their own but others are used mainly or only synergists, acting to increase the effect of other types of flame retardants.

According to the way in which they are incorporated to the polymers flame retardants are classified into two main categories: additives, which are mechanically blended with the polymeric substrate, and reactives which are chemically bound to the polymer either by simple copolymerization or by modification of the parent polymer.[36] However the physical incorporation of additives has several disadvantages.[41] Flame retardant additives may be leached from the polymer, particularly if used for external applications, or may even volatilize during use. They also have to be used in significantly high concentrations in order to be effective, which may in turn affect the physical and mechanical properties

of the polymer. The alternative strategy of using reactive flame retardants is more effective. The relatively low loadings required to achieve sufficient flame retardance do not produce big changes in physical and mechanical properties of the polymer.[42] Furthermore, the flame retardant is then not easily lost from the polymer.

Additionally, and according to environmental issues, flame retardant compounds can also be classified in halogenated and halogen-free flame retardants. The flame-resistance efficiency of halogen-containing flame retardants is high in most cases but due to its halogenated nature they do not decompose naturally so they accumulate in the environment producing serious pollution problems. For this reason, most halogen-containing flame retardants are forbidden now, especially in Europe. Halogen-free flame retardants have been attracting increasing attention from both the academic and industrial communities because of their many advantages, including low toxicity, low smoke production and no release of corrosive gases.

The concept of sustainable development requires fire technologies to be developed which have minimum impact on health and the environment through the life cycle of the material; that is to say, its synthesis, fabrication, use, recycling and disposal. The incorporation of silicon or boron or phosphorus functionality in the polymeric structure is recognized as one of the most efficient ways to obtain an environmentally friendly flame-retardant system.[42] The use of silicon- and boron-containing species as reactive modifiers are far less investigated than phosphorus species.

Phosphorus-based fire retardants

The range of phosphorus-containing flame retardants is extremely wide and the materials versatile, since the element exists in several oxidation states.[36] Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphates are all used as flame retardants. Phosphorus-based flame retardants can be inorganic, organic, or elemental (red phosphorus), can be active in the vapor phase or in the condensed phase, and sometimes may operate simultaneously in both phases.[43]

Phosphine oxides[44] and phosphonates[45,46] have been reported to act in the gas phase through the formation of PO· radicals (reactions [5] to [8]), and PO$_2$·, HOPO·, and HOPO$_2$· radicals respectively, which terminate the highly active flame-propagation radicals (HO· and H·). 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.[46]

[5] (P) $\longrightarrow$ PO· + P· + P$_2$

[6] PO· + H · = HPO

[7] HO · + PO· = HPO + ·O·

[8] P$_2$ + PO· = PO· + P· and so on...
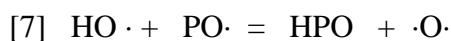
In the condensed phase mechanism, the phosphorus FR is thermally

decomposed giving phosphoric acid (reaction [9]), which is further dehydrated to polyphosphoric acid (reaction [10]).

[9] $P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$

[10] $n\ H_3PO_4 \longrightarrow HO \left(\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}} - O \right)_n H + n\text{-}1\ H_2O$
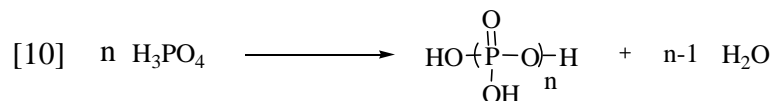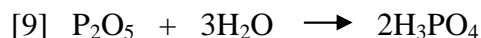
Polyphosphoric acid esterifies and dehydrates the polymer giving rise to unsaturated carbonous species that make up a residue that protects the polymer surface from further degradation (Figure 6).
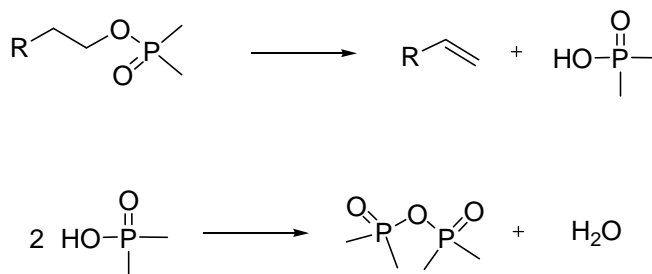
Figure 6. Condensed phase action.

In this way, increasing research is now being directed at the synthesis of phosphorus-based flame retardant polymers. Some recently published examples include polyphosphonates;[47] phosphonate-based polyurethanes;[48] epoxy resins,[49] and polymethacrylates;[50] phosphate-containing nylon[51], silk[52] and polyacrylates;[53] modification of cotton fabric with phosphoric acid;[54] phosphine oxide-based epoxy resins[55] polybenzoxazines,[56] polyethers,[57] spiroorthoesters[58] and poly(ether

ketone)s;[59] DOPO- (9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) containing epoxy resins,[60,55d] polybenzoxazines,[61] polyesters[62] and polyethers.[57] Other examples are ionomer polyesters,[63] polyphosphorinanes,[64] ABS and polystyrene foams.[65]

Boron-based fire retardants

Boron compounds are currently used in textiles and in some plastic formulations as flame retardants.[66] Borax and boric acid have been well established as flame retardants for some considerable time.[67,68] However, there appear to be no reports of any systematic studies of the flammabilities of boron-modified polymers. Although the exact mechanism of action of borates, which are typically used as flame retardant, is unknown, it is believed that they form a borate glass on heating at high temperature. This borate glass acts as a thermal insulating layer to protect the remaining plastic from further oxidative degradation. Furthermore, a carbon-based char or boron carbide-type char may be formed under the glass layer. Most of boron-containing flame retardants decompose thermally giving metaboric acid and boron oxide (Figure 7).

$$2H_3BO_3 \xrightarrow[-2H_2O]{120\text{-}130^{\circ}C} 2HBO_2 \xrightarrow[-H_2O]{260\text{-}270^{\circ}C} B_2O_3$$

Figure 7. Thermal decomposition of boric acid.

Boronic acids [$R-B(OH)_2$] are known to release water on thermolysis, thereby leading to boroxines $(RBO)_3$.

Some examples found in recent literature include the synthesis of boron-containing epoxy-novolac resins,[69] boron-modified phenol-formaldehyde resins,[70] boron-containing phenolic resins,[71,72] the polymerization of boron-containing styrenic monomers[73], the synthesis of organic-inorganic hybrid boron-containing nanocomposites[74] and polyurethane-zinc borate composites.[75]

Silicon-based fire retardants

The use of silicon compounds as reactive components in flame-retardant systems seems to have been little explored, despite their relatively low combustibility. Almost all forms of silicon have been explored as flame retardants but recently there have been a big interest in the use of polyhedral oligomeric silsesquioxanes (POSS) as both additives and reactive components in thermoplastics and thermosets.[76]

Generally, a condensed-phase mechanism which involves a silicon-based protective surface layer is proposed.[77] Most of these systems do not enhance formation of carbonaceous char. Thus, it is proposed that there exists a subset flame retardant mechanism within the general class of "char-enhancing flame retardants" in which high-performance char barrier forms. This high-performance char acts as an insulator and mass-transport barrier, but does not retain additional carbon in the condensed

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phase. Indeed, this is an advantage for this type of fire retardants, because many countries are now recycling via pyrolysis processes, which cause depolymerization and yield useful hydrocarbon feedstocks. Several of these approaches not only offer improved physical properties and recyclability.

Some recently published examples include the synthesis of silicon-containing epoxy resins,[78,79] and polybenzoxazines;[80] the development of siliconized epoxy resin coatings and [81] the synthesis of an alkoxysilane functionalized polycaprolactone/polysiloxane modified epoxy resin through sol-gel process.[82] Furthermore, silicon-based nanocomposites have been prepared via sol-gel method,[83] using polyhedral oligomeric silesquioxane (POSS),[84] polymer-layered silicate nanocomposites[85] and silicone-based materials[86]

Flammability tests

As a consequence of the complex nature and poor reproducibility of fire, there are many techniques for estimating the flammability of polymeric materials.[87,88] Each technique concentrates on certain characteristics of complex combustion process, for example, the ease of heat release, and smoke obscuration.[89] There are three main categories of tests procedure: samall-scale tests in which a small amount of sample is burnt and the combustion behaviour observed, medium scale techniques involving tunnel tests and radiant panel tests, and the large scale room

and corridor experiments. Although the large scale tests are very comprehensive and give the closest representation of a real fire situation, they are expensive and difficult to control and thus the small and medium scale tests are often more practical.[87]

The most widely used laboratory test is the limiting oxygen index (LOI) technique. The high concentrations of oxygen involved with the use of LOI technique are unrepresentative of a real fire, and generally there is a lack of correlation between most of the small-scale tests and the full-scale tests. Recently several novel techniques for measuring a range of properties that correlate well with the full scale tests have been developed.[90] The most useful of these is undoubtedly the cone calorimeter.

- **UL-94 test**

UL-94 is the standard applied by the American Underwriters Laboratories for testing the flammability and fire safety of plastic materials used in devices and appliances.[91] The standard classifies plastics according to the way they burn in various orientations and thicknesses. UL-94 applies not only to the electrical industry but also to all areas of applications except the use of plastics in building. UL-94 is particularly significant for plastics used in electrical products since a UL listing of the product frequently requires a favourable flammability classification of the materials used.[92] UL-94 contains test procedures for both horizontally and vertically positioned test specimens in the form of bars. In the UL-94 HB (Horizontal Burning) test, the burning of a

horizontal plastic specimen is tested, and in the most demanding HB, specifications are: slow burning on a horizontal specimen; burning rate < 76 mm/ min for thickness < 3 mm. In UL-94 V (Vertical Burning) tests, the test specimen is vertical and ignited by a Bunsen burner to be classified according to their burning times as V-0, V-1, V-2. These tests are more rigorous than the HB test since the vertical specimens are burned by their lower ends, thus preheating material above it, and the samples must extinguish themselves. The test layout is illustrated in Figure 8. A flame is applied twice to the lower end of the vertically suspended test specimen for 10 s. The top class, i.e. V-0 is achieved if the mean inter-flame time of five samples after 10 applications of the flame does not exceed 5 s. The material is placed in class V-1 if the mean after-flame time is less than 25 s. If flaming drippings occur, the material is classified in V-2; the ignition of surgical cotton placed below the specimen serves as a criterion for this phenomenon.
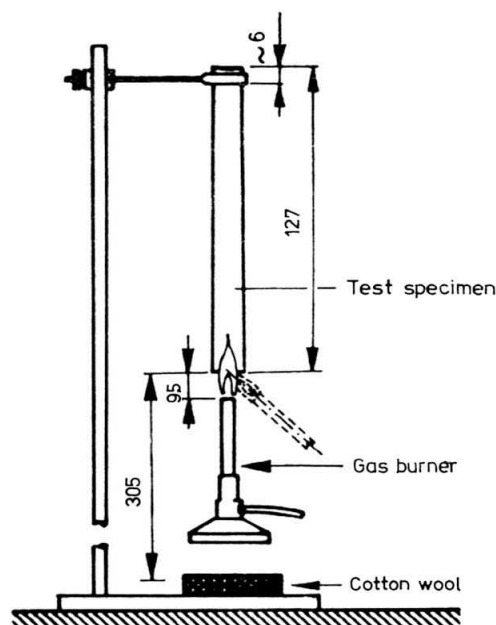
Figure 8. Scheme of UL-94 equipment.

- **Limiting oxygen index (LOI) test**

   The limiting oxygen index (LOI) or oxygen index (OI) is a method or evaluation of the flammability of materials. LOI is defined as the minimum concentration of oxygen in an oxygen–nitrogen mixture, required to sustain combustion of a vertically mounted test specimen. Hence, higher LOI values represent better flame retardancy.[93] The oxygen index is determined by the US standard ASTM D 2863-77[94] procedure which has been introduced as Nordtest method NT Fire 013. Figure 9 shows the principle of the measurement and a figure of LOI test equipment.
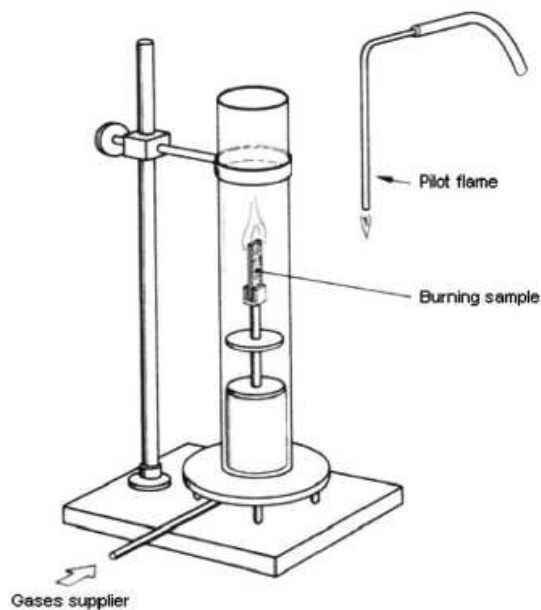
Figure 9. Installation scheme of LOI test equipment.

- **Cone calorimeter**

The Cone Calorimeter is a special research tool to understand the burning characteristics and decomposition/combustion of polymers under the range of conditions permitted in the cone calorimeter. In addition to normal, standard test cone measurements, a range of special research tools are available including techniques to probe into the flame and decomposition zones and extract samples for analysis under both normal and restricted burning conditions. The cone calorimeter test is at present the most advanced method for assessing materials' reaction to fire. Indeed, this test gives a possibility to evaluate: (i) the ignitability; (ii) the combustibility; (iii) the smoke production

and (iv) the production of toxic gases. Figure 10 shows the principle of the cone calorimeter, based on the principle of oxygen consumption calorimetry. Generally, the heat of combustion of any organic material is directly related to the amount of oxygen required for combustion in which 13.1 MJ of heat is released per kg of oxygen consumed. The cone calorimeter brings quantitative analysis to materials flammability research by investigating parameters such as heat release rate (HRR), time to ignition (TTI), total heat release (THR) and mass loss rate (MLR).
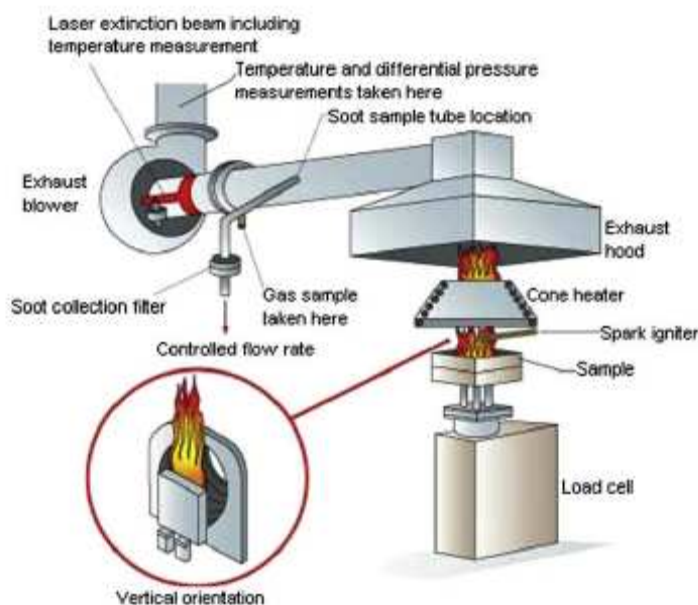
Figure 10. Schematic principle of cone calorimeter.

The HRR measurements can be further interpreted by looking at average HRR, peak HRR and time to peak HRR. Heat release rate is the key measurement required to assess the fire hazard of materials and products as it

quantifies fire size, rate of fire growth and consequently the release of associated smoke and toxic gases. The cone calorimeter, if so configured, can also measure and quantify smoke output as well as CO/CO_2 release rates.[95] Cone calorimeter tests can be conducted in accordance with national and international standards including BS 476 (Part 15), ASTM E1354 and ASTM E1474, and ISO 5660-1. An example of cone calorimeter test according to ISO 5660-1:1993 is given hereafter.[96] The surface of the test specimen is exposed to a constant level of heat irradiance, within the range 0–100 kWm^{-2}, from a conical heater. Volatile gases from the heated specimen are ignited by an electrical spark igniter. Combustion gases are collected by an exhaust hood for further analysis. This gas analysis makes it possible to calculate heat release rate and to assess production of toxic gases from the specimen. Smoke production is assessed by measuring attenuation of a laser beam by smoke in the exhaust duct. The attenuation is related to volume flow, resulting in a measure of smoke density called smoke extinction area [m^2 s^{-1}]. The specimen is mounted on a load cell which records the mass loss rate of the specimen during combustion. A throrough analysis requires testing at several irradiance levels. Typical levels of irradiance are 25, 35, 50 and 75 kWm^{-2}. According to ISO 5660-1:1993(E), three specimens shall be tested at each heat flux level. The test result contains information about dimensions, pre-treatment and conditioning of the test specimens, and information about the test conditions. The following test results are tabulated: (i) time to ignition [TTI, s]; (ii) total heat released [THR, MJm^{-2}], (iii) maximum heat release rate [MHR, kWm^{-2}], (iv) average heat release rate after 180 s and after 300 s [average HRR180, or average HRR300, kWm^{-2}], (v) effective heat of combustion [EHC, MJ kg^{-1}]; (vi) average smoke production [m^2 s^{-1}], (vii)

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production of carbon monoxide (CO) [g]. It is also possible to measure production of other gas components, like cyanhydric acid (HCN). The following results are given graphically for each of the applied irradiation levels: (i) heat release rate [HRR, kWm^{-2}]; (ii) rate of smoke production [m^2 s^{-1}]; (iii) rate of production of CO and HCN [g s^{-1}]; (iv) specimen mass as a function of time [g s^{-1}]. The unit m^2 is related to specimen area. The surface of the specimens shall be essentially flat. The specimens shall be representative of the product, and as far as possible be similar to the final product. A complete test requires that at least 12 specimens with dimensions of 100 mm X 100 mm and of maximum thickness of 50 mm be tested. Different types of typical burning behaviour give rise to characteristic curves of HRR vs. time. Some are illustrated in Figure 11.[97]
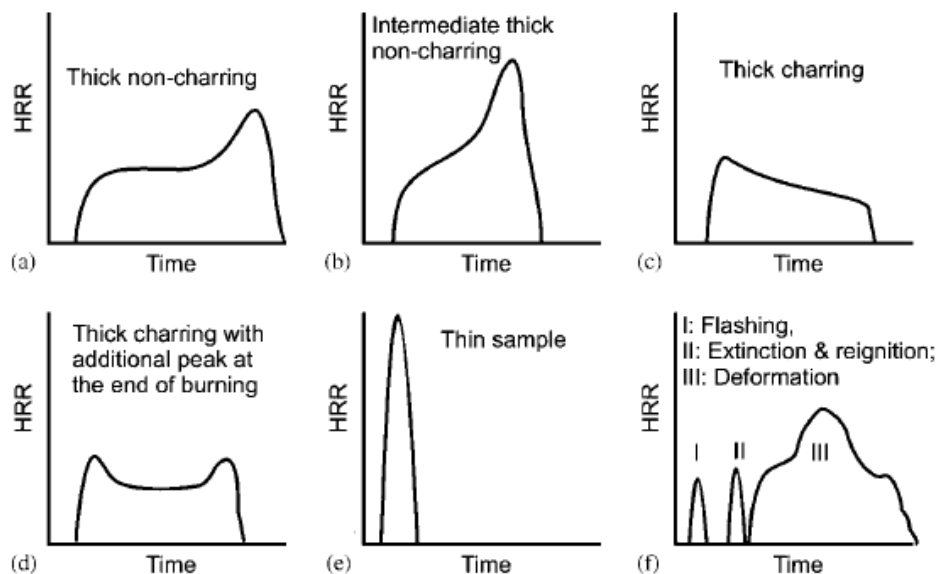
Figure 11. Typical HRR curves for different characteristic burning behaviours.

- **Relation between LOI, cone calorimeter and UL-94 tests**

Since cone calorimeter measures flammability in different manner than LOI and UL-94 fire tests, one should not be surprised by the poor correlation between them. Morgan and Bundy[96] tried to explain differences among LOI, cone calorimeter and UL-94 test. LOI is a small-scale test that uses a variable percentage oxygen atmosphere to maintain a candle-like burn, and UL-94 V applies a small calibrated flame twice under the sample (configured vertically) for 10 s followed by measuring time to extinguishment after each flame application. Cone calorimetry, on the other hand, uses a forced combustion in which radiant heat is projected onto a sample before ignition and during burning of the sample. The sample is usually in a horizontal configuration, thus eliminating any physical effects of polymer burning (dripping away from the flame, for example) that are sometimes used to pass the UL-94 V test, especially under the V-2 rating. Further, the sample in the cone calorimeter exposed to continuous heat during the test is well ventilated, whereas UL-94 is not. In effect, cone calorimeter measures the material response to constant fire threat with time, whereas UL-94 measures the material response to remove a fire threat and its time to self-extinction. Therefore, some studies have been conducted to show correlations between UL-94, LOI and cone calorimeter tests.

1.4. Minimizing energy use: microwave-assisted polymer synthesis

Introduction

Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

Most chemical processes use thermal sources of energy originated from fossil fuels. The energy input to the process is non-specific, i.e. it is not directly targeted at the chemical bonds, or even the molecules undergoing reaction. Much of this energy is wasted in heating up reactors, solvent and even the general environment.

For some processes alternative, more specific, forms of energy such as photochemical, sonochemical and microwave energy may be beneficially applied. Whilst use of such alternative forms of energy is not new they are currently being taken more seriously by manufacturing industries and hence can be viewed as emerging technologies. From the green chemistry point of view this interesting techniques falls into reducing energy in a molecular level in the chemical reaction and will lead to selected future processes being more energy efficient as well as cleaner.

Microwave irradiation is becoming an increasingly popular method of heating samples in the laboratory. It offers a clean, cheap convenient method of heating which often results in higher yields and shorter reaction times. Despite its popularity, and an increasing amount of literature on the subject, microwaves remain an area of mystery for many scientists.

The use of microwave irradiation has become a common heat source in

organic chemistry. Inspired by this enormous success, the use of microwave irradiation is also increasingly studied for polymerization reactions. A large number of examples of reactions have been described in organic synthesis.[98-101] The main areas in which the use of microwave irradiation has been explored in the recent years are step-growth polymerizations, ring-opening polymerizations as well as radical polymerizations.[102]

Direct and rapid heating by microwave irradiation in combination with sealed vessel processing in many cases enables reactions to be carried out in a fraction of the time generally required using conventional conditions. This makes microwave chemistry an ideal tool for rapid reaction scouting and optimization of conditions, allowing very rapid progress through hypotheses–experiment–results iterations. The speed at which multiple variations of reaction conditions can be performed allows an early discussion.

In many of the published examples, microwave heating has been shown to dramatically reduce reaction times, increase product yields, and enhance product purities by reducing unwanted side-reactions compared with conventional heating methods. The advantages of this enabling technology are exploited not only in organic and medicinal chemistry/drug discovery, but have also penetrated related fields such as polymer synthesis, material sciences, nanotechnology, and biochemical processes. At least in the field of organic synthesis, the use of microwave irradiation has become such a popular technique that it might be assumed that, in a few years, most synthetic chemists will probably use microwave energy to heat chemical reactions on a laboratory scale.

Microwave heating is based on dielectric heating; i.e., molecules exhibiting

a permanent dipole moment will try to align to the applied electromagnetic field resulting in rotation, friction, and collision of molecules and, thus, in heat generation. As a result, the heating rate and efficiency of microwave heating strongly depends on the dielectric properties and the relaxation times of there action mixture, whereby the use of good microwave absorbing solvents results in very fast heating.[103] Besides the advantages of fast and homogeneous heating as well as the possible high-temperature chemistry, non-thermal microwave effects due to specific heating of polar intermediates have been observed, e.g., leading to modified selectivities and enabling reactions that cannot be performed with thermal heating.[104] These non-thermal microwave effects are thought to arise from specific microwave absorption by polar components of a reaction making them more reactive under microwave irradiation when compared to thermal heating.

Microwave heating background

Microwaves are electromagnetic waves in the frequency range of 0.3 to 300 GHz, which corresponds to wavelengths of ~1m to 1 cm, respectively. This region of the electromagnetic spectrum lies between the far infrared and radio frequencies.

Radiation of this frequency only affects molecular rotation and is not strong enough to break chemical bonds. Because equipment is widely available to efficiently generate microwaves at this frequency, it is a convenient method for heating microwave absorbing substances. Microwaves, being of an electromagnetic nature, consist of time-varying electric and magnetic fields, and propagate through space at the speed of light. However, the magnetic

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part of the electromagnetic waves does not interact with organic media and, thus, will not participate in microwave heating for most chemical transformations. The capability of a compound to convert microwave irradiation to heat is given by the loss tangent, $\tan(\delta)$:

$$\tan(\delta) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)}$$

in which ε_1 is the permittivity, ε_2 is the dielectric loss factor, and ω is the frequency. The higher $\tan(\delta)$ is at 2.45 GHz, the better the compound will absorb microwaves, resulting in better heating. Consequently, polar substances are expected to heat up more efficient than non- or less polar counterparts. In general, the dielectric loss factor of a solvent determines its ability to absorb microwave energy. The power dissipation by the dielectric material is proportional to this loss factor (ε_2). However, dielectric properties are in general strongly frequency and temperature dependent and, unfortunately, the optimal frequency for most efficient heating shifts further away from 2.45 GHz on heating.[105]

Some recently published examples of polymerization with microwaves include free radical polymerization of styrene,[106] copolymerization of styrene and MMA,[107] preparation of graft-copolymers by free radical polymerization of vinylic monomers,[108] preparation of composites by free radical polymerization,[109] emulsion polymerization[110] and polymerization of oxazolines.[111] Some epoxy resins[112,113] and curing agents[114-116] have also been studied, showing that microwave irradiation is a promising and versatile method to achieve the curing of epoxy materials with considerable reduction of the curing time.

1.5. Safer synthetic methodologies: olefin metathesis

Green chemistry is not a particular set of technologies, but rather an emphasis on the design of chemical products and processes. In some cases, green chemistry takes place at the molecular level to reduce or eliminate the use and generation of hazardous substances. This approach offers environmentally beneficial alternatives to more hazardous chemicals and processes, and thus promotes pollution prevention.

Green chemistry can lead to dramatic changes in how we interact with chemicals on a daily basis as in the case of the 2005 Nobel Prize in Chemistry. Grubbs, Schrock and Chauvin were awarded this price for their contributions to the development of the metathesis reaction in organic synthesis. In the metathesis reaction (from greek, *change-places*), double bonds are broken and made between carbon atoms in ways that cause atom groups to change places. This happens with the assistance of special catalyst molecules. Metathesis is used daily in the chemical industry, mainly in the development of pharmaceuticals and of advanced plastic materials. Thanks to the Laureates' contributions, synthetic methods have been developed that are

- efficient (fewer reaction steps, fewer resources required, less wastage)
- simple (the catalysts are stable in air, at normal temperatures and pressures)
- environmentally friendly (work under bulk conditions or in non-injurious solvents, less hazardous waste products).

The hazardous waste reduction represents a great step forward for the achievement of the 'green chemistry' objectives, which can be accomplished through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment.

In the last years, olefin metathesis has become one of the most powerful synthetic methods.[117] Although double-bond scrambling reactions were initially reported in the mid-1950s,[118] and Banks and Bailey from Philips Petroleum conducted the first research on olefin metathesis and its industrial application in 1964,[119] it was not until 1967 that Calderon and co-workers recognized that both ring-opening polymerization and the disproportionation of acyclic olefins were the same reaction. They coined the term "olefin metathesis" (from greek, changing or exchanging positions).[120] As shown in figure 12, this transformation has a variety of applications.

The illustrated examples include ring-opening metathesis (ROM), ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis polymerization (ADMET), and cross-metathesis (CM). These reactions have enabled the synthesis of an impressively wide range of unsaturated molecules which were challenging or even impossible to prepare by any other means.

From the mid-1950s to the early 1980s, all olefin metathesis was accomplished with poorly defined, multicomponent homogeneous and heterogeneous catalyst systems. These systems consisted of transition metal salts combined with main group alkylating agents or deposited on solid supports. The utility of these catalysts, however, was limited by the harsh

conditions and strong Lewis acids that they required and that made them incompatible with most functional groups.[121]
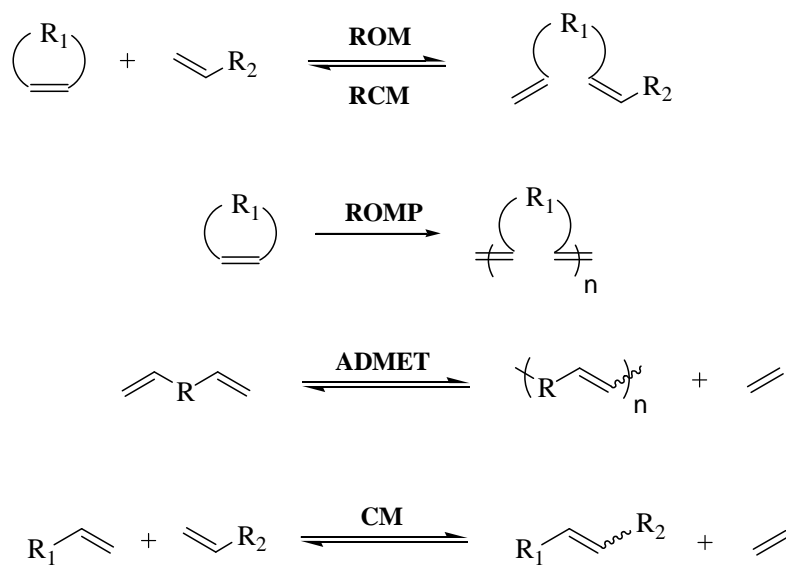
Figure 12. Various metathesis reactions.

Extensive work was done to overcome these problems and to better understand this transformation. The mechanism of the reaction remained unknown until 1970, when Chauvin proposed that the key step in the reaction involves the formation of a metallocyclobutane ring intermediate from a metal carbene and an alkene (Figure 13).[122]
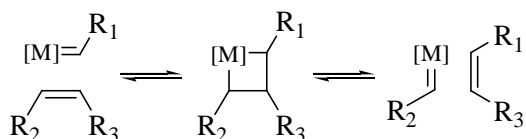
Figure 13. Mechanism proposed by Chauvin and Herisson.

The discovery of the mechanism of olefin metathesis eventually led to the rational design of progressively more advanced, well-defined catalyst systems. A significant breakthrough occurred in 1990 with Schrock's discovery of the well-defined, single-site tungsten and molybdenum alkylidene catalysts.[123] However, these early transition metal based complexes are highly oxophilic, making them susceptible to air and moisture poisoning if they are not employed under rigorously dry, oxygen-free conditions. They are also relatively intolerant to many functional groups, such as alcohols, aldehydes, and carboxylic acids. These factors limited the use of early transition metal-based catalyst for the metathesis of certain functionalized olefins, and thus, the key to improved functional group tolerance in olefin metathesis was the development of catalysts reacting preferentially with olefins in the presence of heteroatomic functionalities. Among the transition metal metathesis catalysts, ruthenium reacts preferentially with carbon-carbon double bonds over most other species, which makes these catalysts unusually stable toward alcohols, amides, aldehydes, and carboxylic acids.

The first well defined ruthenium based metathesis catalyst (**1**, figure 14), developed by Grubbs in the early 1990s, permitted the application of the olefin metathesis reactions in presence of a wide variety of functional groups.[124,125] The metathesis activity as well as the functional group tolerance of these catalysts was further improved by the substitution of one of the trialkyl phosphine ligands by a N-heterocyclic carbene (NHC),[126] leading to the second generation Grubbs catalysts (**2** and **3** are shown as representative examples in figure 14).[127] Thus, with the introduction of highly active and robust metathesis catalysts, the number of polymeric structures available

through the design of new monomers has ever since increased.
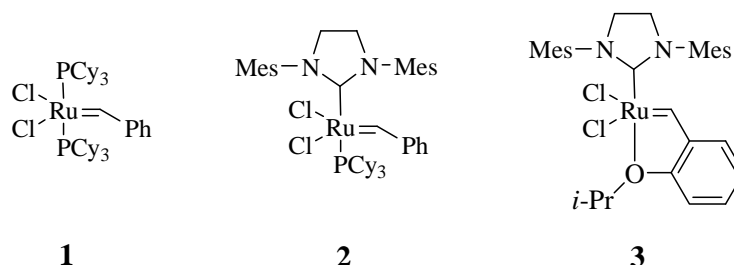
Figure 14. Grubbs 1st generation (**1**), Grubbs 2nd generation (**2**) and Hoveyda-Grubbs 2nd generation (**3**) metathesis catalysts.

Cross-metathesis

Olefin cross metathesis (CM) is a convenient route to functionalized and higher olefins from simple alkene precursors. Cross metathesis has recently gained prominence due to the development of new catalysts that have expanded the variety of functional groups amenable to CM and have demonstrated the ability to prepare highly substituted olefins by CM,[121] often in a stereoselective manner. However, cross metathesis remains an underrepresented area of olefin metathesis when compared to ring-opening metathesis polymerizations (ROMP)[128] and ring-closing metathesis (RCM).[129] This has been predominantly a result of several factors: first, the low catalyst activity to effect a reaction without a strong enthalpic driving force (such as ring-strain release in ROMP) or the entropic advantage of intramolecular reactions (such as RCM), second, the low product selectivity for the CM product, and, third, the poor stereoselectivity in the newly formed

olefin. A general scheme illustrating the mechanism of cross-metathesis is depicted in Figure 15.
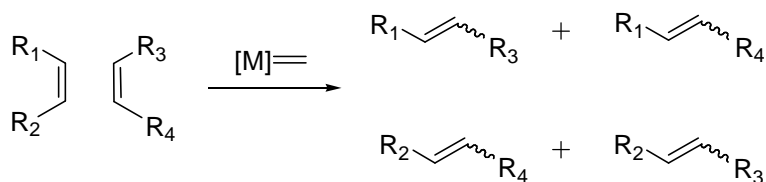
Figure 15. General mechanism for catalytic cross metathesis.

Olefin metathesis with oleochemicals is a well-established field of research.[130] Traditionally, fatty-acid derivatives were only investigated in self-metathesis reactions and cross-metathesis reactions with unfunctional olefins (such as ethylene). However, the recent development of new metathesis catalysts and reaction conditions now allows their reaction with a variety functional group containing cross-metathesis reaction partners to yield α,ω-difunctional compounds with low catalyst loadings and high conversions.

As for the self-metathesis, Boelhouwer *et al*. reported the first cross-metathesis reaction involving oleochemicals in 1972.[131] The most frequently investigated cross-metathesis reaction in the field of oleochemistry is the so-called ethenolysis, the cross-metathesis with ethene.[132] Another more frequently reported cross-metathesis reaction partner for fatty acid derivatives is 2-butene.[133-135] However, little is known about the cross-metathesis of fatty acid derivatives with reaction

partners that bear functional groups. So-called libraries of internal olefins were prepared by the self and cross-metathesis of a variety of derivatives of oleic acid, leading to the expected statistical mixtures of differently substituted olefins.[136]

The first cross-metathesis reaction of unsaturated fatty acid methyl esters with methyl acrylate, leading to long chain diesters, was reported in 2007.[137] Other examples found in recent literature include the cross-metathesis of fatty acid methyl esters with acylonitrile,[138] and allyl chloride[139] to yield α,ω-diesters, ω-cyano-esters, and ω-chloroesters, the cross-metathesis of fatty alcohols with methyl acrylate[137] or the cross-metathesis of fatty acid derivatives with alkynes[140] (ene-yne cross-metathesis). An added value to the development of these reactions is the low catalytic amounts required. In this respect, in a recent example, the cross-metathesis product of the reaction between methyl 10-undecenoate and methyl acrylate was obtained in 82% yield with a catalyst load of 0.5%.[141] Moreover, olefin cross-metathesis has been reported as an efficient approach to prepare bioconjugates of an amino acid, a fatty acid and a sugar moiety.[142] Recently, the cross-metathesis of a variety of monounsaturated fatty acids with different chain lengths and positions of the double bond with methyl acrylate was investigated in detail. Furthermore, the cross-metathesis reactions with fatty acid derivatives enable the synthesis of a variety of renewable monomers for the development of many different kinds of polymers, including, e.g, polyesters, polyamides, polyethers as well as polyolefins.[143]

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OBJECTIVES

The purpose of the study reported in this thesis was to develop new fire retardant biobased thermosets from vegetable oils as renewable resources. To achieve this goal, the experimental work was focused on exploiting the reactivity of the internal double bonds of soybean oil.

The general objective of this thesis is the preparation and characterization of halogen-free soybean oil thermosets with enhanced flame retardant properties to achieve safer materials. In this way, the synthesis by cationic copolymerization of soybean oil, styrene and divinylbenzene with different silicon, boron or phosphorus-containing comonomers has been carried out.

The minimization of energy use has been considered by studying this cationic copolymerization using microwave irradiation.

The use of metathesis reactions as an efficient way to more reactive monomers has been considered in the synthesis of phosphorus-containing monomers, which were copolymerized with soybean oil to infer flame retardant properties to the final thermosets.

A detailed study of the flame retardance behaviour of some thermosets has been carried out using cone calorimeter.

All the above objectives fall into the four main challenges of Green Chemistry.

2. *Experimental Procedures and Results*

2.1. Silicon-Containing Soybean-Oil Based Copolymers: Synthesis and Properties

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Marta Sacristán Benito
ISBN:978-84-693-1532-3/DL:T-649-2010

Biobased copolymers 63

Silicon-Containing Soybean-Oil Based Copolymers. Synthesis and Properties

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ABSTRACT

New silicon containing soybean oil based copolymers were prepared from soybean oil, styrene, divinylbenzene and p-trimethylsilylstyrene by cationic polymerization using boron trifluoride diethyl etherate as initiator. Soxhlet extraction and NMR spectroscopy indicate that the copolymers consist of a crosslinked network plasticized with varying amounts of oligomers and unreacted oil. This soluble fraction increases when the SiST content in the feed increases, according to a lower reactivity of this monomer. The thermal, dynamomechanical and flame retardant properties of these materials were examined. Thermosets with glass transition temperatures ranging from 50 to 62ºC, which are thermally stable below 350ºC, and with LOI values from 22.6 to 29.7 were obtained. Their properties suggest that these materials may provide useful alternatives to current non renewable based thermosets and that the flame retardant properties of vegetable oil based thermosets can be improved by adding covalently bonded silicon to the polymer.

Keywords: biopolymers, vegetable oils, renewable resources, silicon.

INTRODUCTION

Recently, there has been strong demand on development of polymeric materials from renewable resources for the contribution of global sustainability without depletion of scarce resources. The growing demand for petroleum based products and the resulting negative impact on the environment plus the scarcity of nonrenewable resources among other factors have stimulated the use of renewable feedstock in academic research and chemical industry.[1] Polymeric materials from cellulose, starch, proteins and natural oils have been described.[2] These biopolymers offer the advantages of low cost, ready availability from renewable natural resources and potential biodegradability. Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds and are now being used in an increasing number of industrial applications, in addition to being a food source for human beings. Recently there have been many attempts to convert vegetable oils and fatty acids to useful polymers.[3]

Vegetable oils are triglycerides of different fatty acids with varying degrees of unsaturation. It is generally considered difficult to polymerize vegetable oils themselves due to their lack of active functional groups. The thermal polymerization of vegetable oils at high temperature under nitrogen atmosphere has been reported to give low molecular weight polymers.[4] Moreover, it has been described that the reactivity of the soybean oil is rather low and its cationic homopolymerization is relatively difficult.[5] However, the presence of double bonds makes possible to attach some functional groups through chemical modification to produce hydroxylated, epoxidized,

maleinized or acrylated triglycerides, which are capable of polymerization. Various chemical pathways for functionalizing triglycerides and fatty acids have been studied.[6-8]

In recent years, extensive work has been done to develop polymers from triglycerides or fatty acids as the main component. The research focuses on improving the physical properties of solid thermoplastic and thermosetting materials because triglyceride-based materials demonstrated low molecular weights and light crosslinking, incapable of displaying the necessary rigidity and strength required for structural applications by themselves.[9] A wide variety of new polymeric materials have been developed by the thermal or cationic copolymerization of natural oils with styrene and divinylbenzene or dicyclopentadiene[10] or from acrylated epoxidized natural oils and styrene.[11] Recently, biobased nanocomposites from vegetable oils with improved mechanical properties, thermal stability and barrier properties have been described.[12-14]

Moreover, like other organic polymeric materials, the flammability of vegetable oil based materials is a shortcoming in some applications. Most of the flame retardant resins used in industry come from petroleum-based chemicals. Kusefoglu *et al*. reported the synthesis and characterization of flame-retardant polymers from bromoacrylated plant oil triglycerides.[15] However, the flame-retardant resins that contain bromine release hydrogen bromide during combustion, which causes corrosion and toxicity. The concept of sustainable development requires fire retardant technologies to be developed which have minimum impact on health and the environment

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ISBN:978-84-693-1992-9/DL:T-1049-2010
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throughout the life cycle of the fire-retardant material: that is to say, its synthesis, fabrication, use, recycling and disposal. These considerations mean that the search is now on new environmentally friendly flame-retardant polymeric materials. Phosphorus- and silicon-containing polymers are well recognized for their flame retardant properties,[16] and they are increasingly becoming more popular than their halogen counterparts, as they generally give off nontoxic combustion products.[17] Therefore, the incorporation of organosilicon functionalities in the polymeric structure is recognized as one of the most efficient ways to obtain an environmentally friendly flame-retardant system. Research has shown that the addition of relatively small amounts of silicon compounds to various polymeric materials has a flame retardant effect. This is partly because these compounds dilute the more combustible organic components and partly because the silicaceus residues can form a barrier to an advancing flame.[18] Thus, to further extend the application of renewable resources and to obtain flame retardant polymers, we have chosen for study industrially promising biopolymers from soybean oil, divinylbenzene and styrene. The present work investigates the influence of adding different amounts of a silicon-containing styrene, p-trimethylsilylstyrene, to the cationic copolymerization of soybean oil, styrene and divinylbenzene. The structure, thermal stability and mechanical and flame retardant properties of the resulting biopolymers have been investigated.

EXPERIMENTAL

Materials

The soybean oil used in this study (iodine value = 135) was supplied by Aldrich Chemical and has been used without further purification. Styrene and divinylbenzene were purchased from Fluka and washed with a NaOH 10% solution and then with water. The distilled-grade boron trifluoride diethyl etherate (BF_3OEt_2) used to initiate cationic polymerization of the soybean oil was supplied by Aldrich. Methyl oleate was purchased from Alfa Aesar and was used to modify the original initiator, boron trifluoride diethyl etherate. The solvents were purified using standard procedures.

Synthesis of 4-trimethylsilylstyrene[19]

To an oven-dried 500-mL round-bottom flask, equipped with a refrigerant and cooled/purged under a stream of N_2 gas were placed in this order: 6.7 g (274 mmol) of Mg, a small amount of I_2, 274 mL of anhydrous THF, 14.9 g (137 mmol) of $ClSiMe_3$ and 25.0 g (137 mmol) of 4-chlorostyrene. This flask was plunged into a commercial ultrasonic cleaning bath (Selecta, 50 Hz, 360 W) and sonicated for 2 h. The mixture was washed with a saturated solution of sodium chloride and extracted with diethylether. The organic layers were dried over magnesium sulphate, the solvents were removed under reduced pressure and the obtained compound was purified by column chromatography (petroleum ether). The yield obtained was 75%.

^{1}H-NMR (CDCl$_3$, δ, ppm): 0.3 (s, 9H), 5.3 (dd, 1H, J=10.8 Hz, J=1.2 Hz), 5.8 (dd, 1H, J=17.6 Hz, J=1.2 Hz), 6.7 (dd, 1H, J=17.6 Hz, J=10.8 Hz), 7.4 (d, 2H, J= 8.0 Hz), 7.5 (d, 2H, J= 8.0 Hz).

^{13}C-NMR (CDCl$_3$, δ, ppm): 0.9 (q), 114.3 (t), 125.7 (d), 133.8 (d), 137.1 (d), 138.1 (s), 140.3 (s).

^{29}Si-NMR (CDCl$_3$, δ, ppm): -4.2

Cationic Copolymerization

The following reaction procedure was usually employed. The desired amounts of 4-trimethylsilylstyrene, styrene and divinylbenzene were added to the soybean oil (Table 1).

The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of a modified initiator (3 mol% of BF$_3$OEt$_2$ based on the total C=C double bond in the polymerization mixture) The modified initiator was prepared by mixing methyl oleate with the original initiator, boron trifluoride diethyl etherate (molar ratio BF$_3$OEt$_2$:MeOL 1.1:1.0). The reaction mixture was then injected into aluminium moulds and heated for a given time at the appropriate temperatures, usually 12 h at 60ºC, followed by 24 h at 110ºC and l 24 h at 140ºC. The yields of resulting polymer were essentially quantitative. The nomenclature adopted in this work for the polymer samples is as follows: SOY represents the regular soybean oil; SiST stands for the 4-trimethylsilylstyrene; ST, DVB represent the styrene and divinylbenzene comonomers respectively (Scheme 1). BFE is the initiator boron trifluoride diethyl etherate and MeOL stands for methyl oleate.

Polymer Extraction

A 0.5 g sample of the bulk polymer was extracted for 24 h with 200 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the

resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble fractions were isolated for further characterization. The insoluble solid was dried under vacuum for several hours before weighing.

Characterization

The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in absorbance mode. An attenuated-total-reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

The NMR spectra of the oil samples were recorded on a Varian Gemini 400-MHz spectrometer (400 MHz for ^{1}H and 100.57 for ^{13}C). The samples were dissolved in deuterated chloroform, and ^{1}H-NMR and ^{13}C-NMR spectra were obtained at room temperature. ^{13}C and ^{29}Si MAS NMR spectra were performed, with finely ground samples, on a Varian Gemini 400 MHz spectrometer at a 79 MHz resonance frequency, MAS being applied with a 20s delay time. ^{1}H HR-MAS NMR spectra were recorded on a Brucker Avance III 500 spectrometer operating at a proton frequency of 500.13 MHz. The instrument was equipped with a 4 mm triple resonance gradient HR-MAS probe. A Brucker Cooling Unit (BCU-Xtreme) was used to keep the sample temperature at 27ºC. Samples prepared with CDCl$_3$ were spun at 6 kHz to keep the rotation side bands out of the spectral region of interest. One-dimensional ^{1}H spectra were acquired in 1 min and 16 scans with a 1.0s relaxation delay.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer with N_2 as the purge gas. The heating rate was 10ºC/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as the purge gas at scanning rates of 10°C/min. Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three point bending configuration. The various thermal transitions were studied between -100 and 100ºC at a heating rate of 3ºC/min and a fixed frequency of 1 Hz.

RESULTS AND DISCUSION

The commercially available soybean oil employed in this study is primarily composed of unsaturated linoleic (C18:2), oleic (C18:1) and linolenic (C18:3) acids as well as saturated stearic (C18:0) and palmitic (C16:0) fatty acids. The content of other saturated and unsaturated fatty acids is negligible. The unsaturated fatty acid content determines the degree of unsaturation and the reactivity of the vegetable oil. The degree of unsaturation, expressed as the number of carbon-carbon double bonds per triglyceride, was 4.7 as obtained from the iodine index value.

The ^{1}H NMR spectrum of soybean oil can be seen in Figure 1. Signal at 5.4-5.2 ppm is characteristic for olefinic hydrogens and for the methine protons of the glycerin backbone.
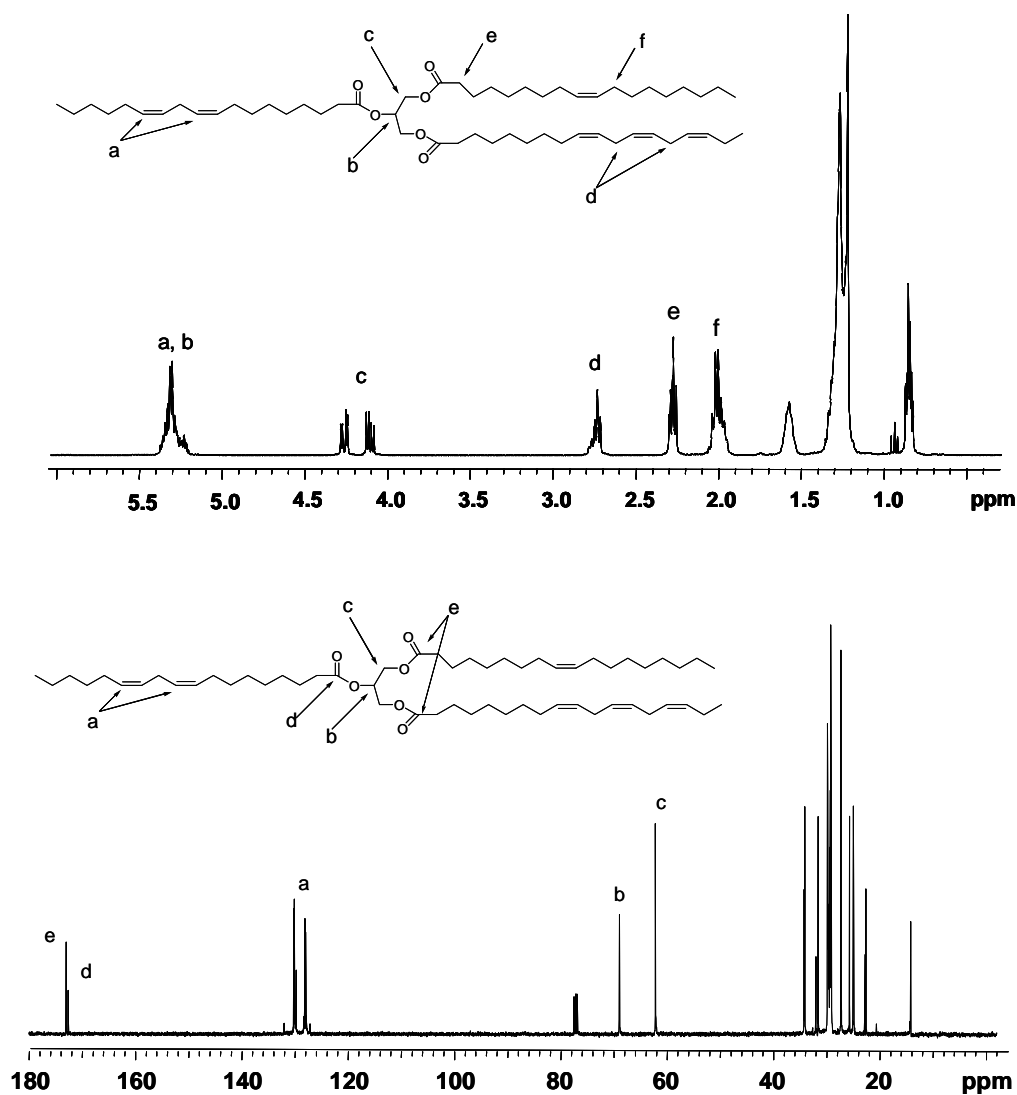
Figure 1. ^{1}H and ^{13}C NMR spectra of soybean oil (CDCl$_3$/TMS, δ ppm).

The signals at 4.2 and 4.1 ppm correspond to the diastereotopic protons of the glycerin methylene units and the multiplet at 2.7 ppm is attributed to the methylene protons between two carbon-carbon double bonds. The signal at 2.3 ppm is assigned to the methylene protons adjacent to the carbonyl groups

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and the signal at 2.1 ppm is characteristic of the methylene protons adjacent to the carbon carbon double bonds.

The degree of unsaturation can be calculated from the area of the signal at 5.4-5.2 ppm and the area of the signal at 4.2-4.1 ppm, giving a value of 4.5 double bonds per triglyceride, in accordance to the value obtained from the iodine index.

Soybean oil was also characterized by ^{13}C NMR spectrum in figure 1. Signals at 173 ppm and 130-128 ppm can be attributed to the carbonylic and olefinic carbons respectively. Signals corresponding to the methine and methylene carbons of the glycerin backbone appear at 69 and 62 ppm respectively.

The cationic polymerization of soybean oils using boron trifluoride diethyl etherate as initiator produces viscous oils. Their reactivity towards cationic homopolymerization is rather low and the initiator has been found to be immiscible with the oil, thus the conversion to high molecular weight polymers has proven relatively difficult. The copolymerization of soybean oils, styrene and divinylbenzene using boron trifluoride diethyl etherate is also heterogeneous, being the poor miscibility between the soybean oil and the initiator the main reason for the heterogeneity rather than the difference in the reactivities between the oil and the styrenic monomers. However, completely homogeneous reaction media can be obtained when the initiator is modified with fish oil ethyl ester or soybean oil methyl esters.[5,9] In our case, the initiator system was obtained by mixing methyl oleate with BFE and homogeneous reactions were generated from a mixture of soybean oil, styrene and divinylbenzene in a molar ratio 1.00:6.00:2.25 (Sample SSD, Table 1). This composition has been chosen because it approximates the

composition of a maximum oil incorporated into the polymer as described in the literature for the cationic copolymerization of SOY/ST/DVB.[5] The amount of BFE was kept constant at 3 mol % based on the total C=C double bond in the polymerization mixture (molar ratio BFE: MeOL 1.1:1.0).

Table 1. Molar ratio of the copolymers.

Sample	Molar ratio SOY/ST/SiST/DVB[a]	Si W%	T onset[b] (ºC)	T max[c] (ºC)	ΔH (KJ/mol C=C)
SSD	1.00/6.00/ - /2.25	-	52	74	20
SSDSi-1	1.00/5.28/0.72/2.25	1	46	70	28
SSDSi-3	1.00/3.72/2.27/2.25	3	55	76	29
SSDSi-5	1.00/2.00/4.00/2.25	5	60	86	29
SSDSi-7	1.00/ - /6.00/2.25	7	64	95	25

[a] 3 mol% of BFE regarding C=C (BFE: MeOL molar ratio 1.1: 1.0)

[b] Temperature of the onset of the crosslinking exotherm (10 ºC/min).

[c] Temperature of the maximum of the crosslinking exotherm (10 ºC/min).

In this work, styrene and 4-trimethylsilylstyrene were used as a major comonomers and divinylbenzene as a crosslinking agent to control the crosslinking density (scheme 1). Recently, a simple and efficient procedure has been developed for the synthesis of *para*-substituted styrenes with groups containing an atom of the 14th group by one pot reaction of halogenosilanes, germanes or stannanes, organic halides and magnesium using ultrasound methods.[19] Using 4-chlorostyrene, magnesium and trimethylsilylchloride, SiST was obtained in 2h with a 75% yield.

SOY

ST   **DVB**   **SiST**
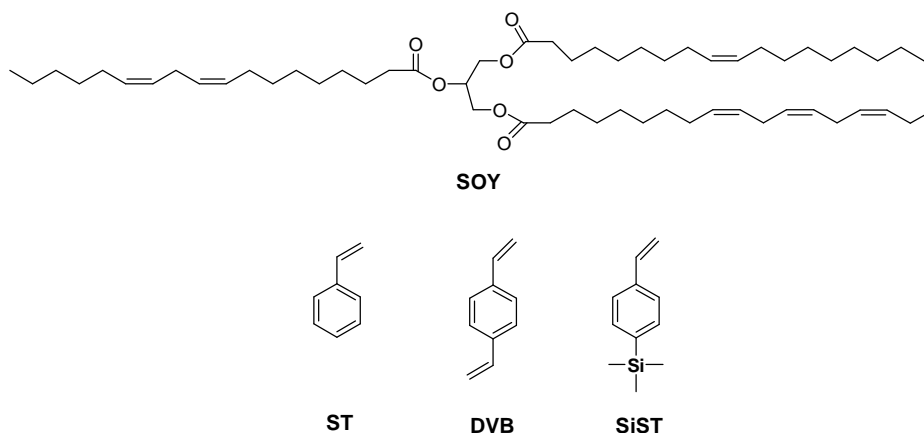
Scheme 1. Structure of the comonomers.

A set of copolymerizations was carried out with compositions shown in Table 1. DVB amount was kept constant as the ST + SiST amount, while the content of ST decreases as the SiST increases to obtain thermosets with different silicon content, from 1 to 7 wt %. The curing reaction was studied by dynamic DSC (figure 2 and table 1) and the plots showed a broad exotherm that shifted to higher temperatures as the SiST content increased. The presence of this comonomer seems to decrease the reactivity of the systems.

It is reported [20] for the cationic polymerization of styrene derivatives, that as the electron-donating ability of the substituents on the styrenic phenyl ring decreases, the reactivity of the monomers decreases, and the reactivity of the corresponding cation increases. The silicon atom acts as a π acceptor, withdrawing the electron density of the phenol ring and decreasing the reactivity of the SiST. Moreover, the increase in the reactivity of the corresponding cation may favor side reactions as isomerization, inter and

intra molecular alkylation, specially the major side reaction of indanic cyclization for the cationic polymerization of styrene derivatives.[21]
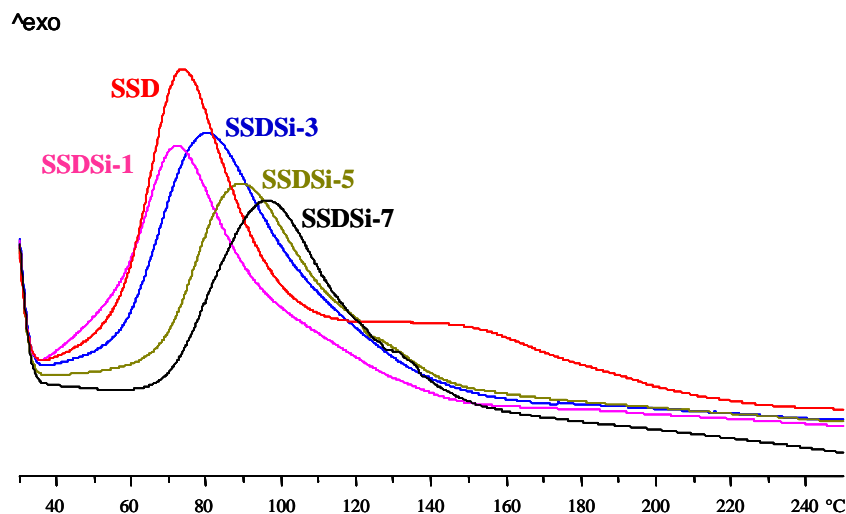
Figure 2. DSC thermograms (10ºC/min) of the curing mixtures.

From the DSC data, curing and postcuring conditions were established as 24h at 110ºC (140ºC for SSDSi-7) and 24h at 140ºC. The fully cured soybean oil copolymers have been obtained in essentially quantitative yields. All the copolymers appear as clear to dark-yellow rubbery materials at room temperature, ranging from tough and ductile to very soft rubbers. FTIR analyses have been performed to characterize the resulting materials. Bands at 1740, 1600 and 1492 cm^{-1} confirm the presence of carbonyl groups and aromatic moieties, respectively, but the existence of unreacted C=C bonds is not detected. ^{13}C MAS NMR spectra confirmed the incorporation of soybean oil and aromatic moieties, by the presence of C=O and C=C signals at 170 and 130 ppm. Moreover, signals attributable to the methyl protons of the (CH$_3$)$_3$Si- moiety can be seen at 0.3 ppm for the silicon containing polymers.

According to the presence of silicon in these polymers, ^{29}Si MAS NMR spectroscopy showed just a single absorption peak at –10.9 ppm.

High Resolution NMR spectroscopy was used as a useful tool to further study of the extent of the crosslinking reaction. Conventional solid NMR spectroscopy usually results in signal broadening due to the lack of molecular mobility. However, HR-MAS NMR spectroscopy reduces significantly this broadening by spinning the sample around an axis oriented at an angle θ= 54.7º with the direction of the magnetic field. The sample is spinned at a rate larger than the anisotropic interactions causing them to be averaged to their isotropic value and therefore, resulting in signal narrowing. To obtain a good spectrum, a solvent must be added to swell the polymer in some extent. However, the swelling is less effective in the sections of the polymer with a higher crosslinking density. As a result, crosslinking sites cannot be seen with the same resolution as the sections with higher mobility. Figure 3 depicts the ^{1}H HR-MAS NMR spectra of samples SSD, SSDSi-3 and SSDSi-5. The spectrum of the silicon free polymer shows a broad signal at 7.5-6.5 ppm corresponding to the aromatic protons of the ST and DVB, signals at 5.5-5.2 ppm, attributed to the vinylic protons and methine protons, and signals at 4.5-4.2 ppm, corresponding to the methylene protons of the soybean. The signal at about 3.6 ppm confirms the presence of methyl oleate as part of the initiator system. Moreover, signals attributed to the methylene protons adjacent to the C=C bonds of the soybean oil can be seen at 2.4 and 2.1 ppm, according to the existence of unreacted moieties. The spectra of the silicon containing polymers are very similar, with the exception of the signal

at 0.3 ppm corresponding to the protons of the trimethylsilyl unit, which increases as the silicon content does.
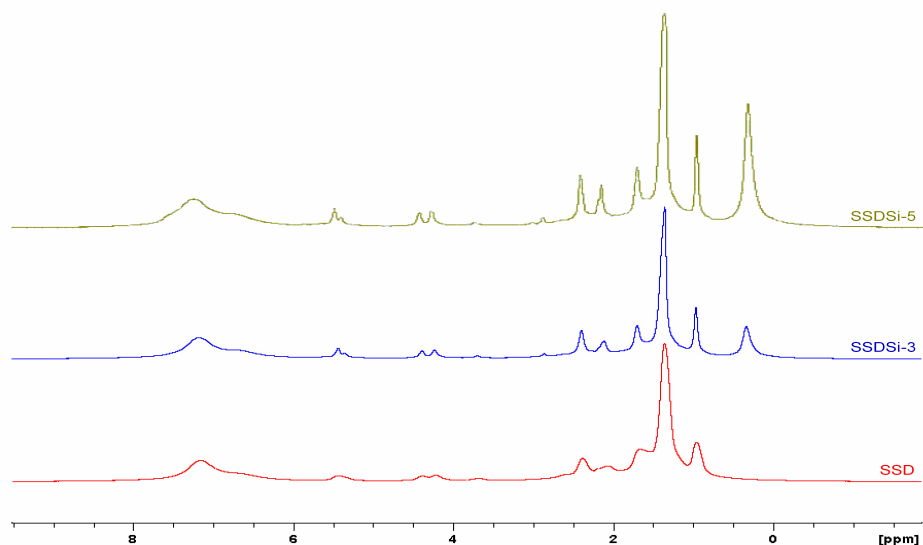
Figure 3. ^{1}H HR-MAS NMR spectra of the copolymers.

The composition of these copolymers have been studied after Soxhlet extraction analysis with methylene chloride as a refluxing solvent. Table 2 summarizes the results from these analysis. Typically after overnight extraction 90-68 wt % of insoluble materials are retained from the bulk materials. The yield of the insoluble material from the SSDSi-7 system is noticeable lower than the one of the SSD system. These results can be due to the lower reactivity of SiST. A change in the concentration of the less reactive comonomer leads to a significant change in the yield of the crosslinked polymer.

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Table 2. Composition of the copolymers.

Sample	Soluble fraction[a] (w %)	Insoluble fraction[a] (w %)	Aromatic material (w %)			Si soluble fraction (w %)
			Feed	Soluble fraction	Insoluble fraction	
SSD	8	92	47	13	87	-
SSDSi-1	17	83	48	14	86	-
SSDSi-3	23	77	51	16	84	0.7
SSDSi-5	25	75	54	23	77	3.0
SSDSi-7	32	68	56	27	73	3.5

[a] Weight percentage of the soluble and insoluble fractions after Soxhlet extraction with methylene chloride.

[b] The weight percentage of aromatic materials in the extracted soluble fraction is calculated calculated from the ^{1}H NMR spectra. Data for the insoluble fraction have been calculated indirectly from these values.

[c] Si content of the soluble fraction from ^{1}H NMR spectra.

The insoluble fractions were characterized by ^{1}H HR-MAS NMR spectroscopy, and the soluble extracts were characterized by ^{1}H NMR spectroscopy. Figure 4 shows the spectra of both fractions for the SSDSi-3 system. As can be seen, the most important difference among them is the relative intensity of signals corresponding to the CH_2 units directly attached to the C=C bonds, at 2.7 and 2.0 ppm, compared to the signals of the CH_2 units attached to the C=O of the carboxylate, at 2.3 ppm, which are lower for the insoluble fraction, according to a major proportion of unreacted C=C triglyceride bonds in the soluble fraction. From the peak areas of the aromatic protons signal (broad signal centered at 7.0 ppm) and the glycerine methylene protons (4.2 ppm) in the ^{1}H NMR spectra of the soluble fractions, it is possible to calculate the molar ratio of the aromatic and oil components present in the soluble extracts, and the results are collected in table 2.
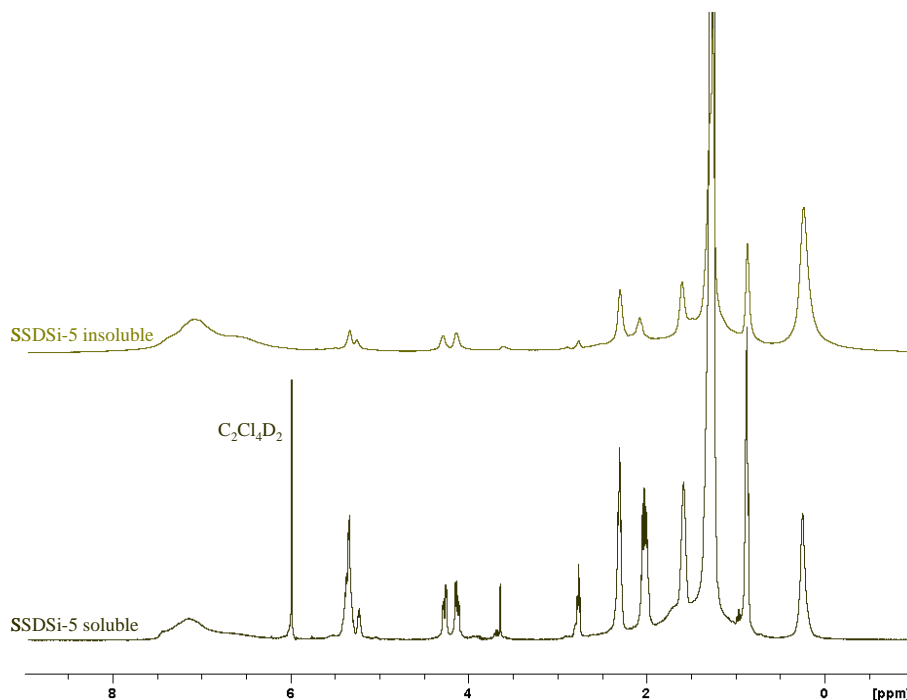
Figure 4. ^{1}H NMR spectrum of soluble fraction and ^{1}H HR-MAS NMR spectrum of insoluble fraction of copolymer SSDSi-5.

As can be seen, the aromatic content of the soluble fraction is in all cases much lower that the expected from the initial copolymerization mixture, and consequently, there is a higher content of aromatic materials in the insoluble fraction. There is an increase in the aromatic part of the soluble fraction when the amount of SiST increases. Taking into account that the initial molar ratio aromatic/oil is a constant value, this should be due to the lower reactivity of this monomer. This hypothesis is also supported by the Si content of the soluble fraction, which has been calculated from the ^{1}H NMR spectra using anisol, as an internal standard, and the signal at 0.3 ppm, corresponding to the

methyl protons directly bonded to the silicon atom and the signal at 3.8 ppm, corresponding to the methoxy protons of the anisol. The Si content in the soluble fraction increases with the SiST initial content, according to the expected behaviour for a less reactive comonomer.

DMA has been used to investigate the dynamic mechanical behavior of the copolymers. Figure 5 shows the storage moduli and the tan δ values of the samples with different silicon contents. At temperatures below -25ºC the copolymers are in the glassy state and their storage moduli decrease slightly with increasing temperature. A rapid decrease in the E' value of roughly 4 orders of magnitude is observed in the temperature range from –20 to 100 ºC, corresponding to the primary relaxation process of the copolymers. The energy dissipation associated to the modulus decrease can be seen as a maximum in the tan δ versus T curve.

The modulus reaches a plateau at higher temperatures which is assigned to the rubbery state. As the SiST content of the copolymers increases, the storage modulus decreases over the entire temperature range, because of the increased amounts of soluble fraction present in the copolymers.

The presence of the rubbery plateau in the DMA curve is evidence for the existence of a stable crosslinked network and according to the kinetic theory of rubber elasticity, the crosslinking density of the copolymer ν can be determined from the rubbery moduli using the following equation

$$E' = 3\,\nu\,RT$$

where E' is the storage modulus of the crosslinked copolymer in the rubbery region above the glass transition temperature, R is the universal gas constant and T is the absolute temperature.
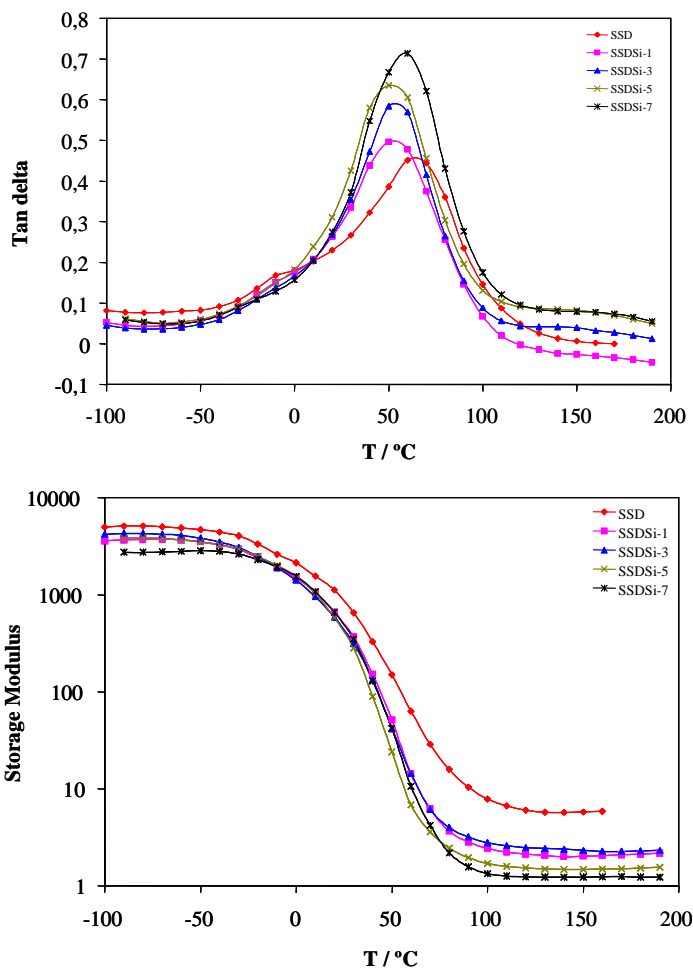
Figure 5. Tan delta and Storage Modulus of the copolymers.

Rubber elasticity theory is not expected to be completely applicable to the highly crosslinked polymers, but should show general trends in how crosslinking density is affected by the SiST content. The values of the storage moduli E' used for calculations were taken at 50ºC above the Tg and are collected in table 3. The crosslinking density of the silicon free sample, 6.6×10^2 mol/m^3, is in the range of the previously described SSD copolymers.[22] It is much higher than those of the silicon containing samples and decreases with the increase in SiST content. Since the storage modulus is a manifestation of the crosslinking density and hence of the network stiffness, this must be due to the higher soluble fraction content reported in table 1, in spite of the higher aromatic content of the insoluble fraction which indicates that the triglyceride arms are decreasingly incorporated into the network as the SiST content increases.

From the tan δ plots of figure 5, the presence of a shoulder in SSD and SSDSi-1 indicates that they have two glass transition temperatures which merge into a very broad transition (Table 3).

The copolymers appear to be complex heterogeneous systems composed of hard aromatic rich phases and soft oil rich phases, with certain amount of oligomers and unreacted monomers which act as plasticizers. The high temperature transition (62º and 57ºC) corresponds to the glass transition temperature of the plasticized aromatic rich phase, while the low temperature transition (-10ºC) is attributed to the plasticized oil rich phase. In contrast, SSDSi-3, SSDSi-5 and SSDSi-7 posses a single glass transition in the range of 56-58ºC, slightly lower than the previous samples.

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The shift of the higher Tg to lower temperatures seems to indicate that the crosslinked polymer becomes more compatible with the oil rich phase and is in accordance to the lower aromatic content of the insoluble fraction.

Table 3. Thermal properties of the copolymers.

Sample	ν_e (mol/m³)[a]	Tg (°C)[b]	Nitrogen			Air					LOI
			$T_{10\%}$ (°C)[c]	T_{max} (°C)[d]	Yield 800°C (%)[e]	$T_{10\%}$ (°C)[c]	T_{max1} (°C)[d]	T_{max2} (°C)[d]	T_{max3} (°C)[d]	Yield 800°C (%)[e]	
SSD	659	-10, 62	378	432	5	349	362	434	582	1	19.2
SSDSi-1	238	57	377	431	4	354	360	433	580	1	22.6
SSDSi-3	282	56	371	428	4	354	363	428	586	1	25.6
SSDSi-5	173	54	367	443	4	346	359	426	613	1	28.6
SSDSi-7	152	58	371	440	3	348	366	424	580	1	29.7

[a] Crosslinking densities have been calculated 50ºC above the corresponding Tg .

[b] Glass transition temperatures are calculated from the maxima of the Tan δ curves.

[c] Temperature of 10% weight loss.

[d] Temperature of the maximum weight loss rate.

[e] Char yield at 800ºC.

The height of the tan δ peaks increases as the amount of SiST does indicating a lower crosslinking density and a higher segmental mobility. With the increase of the SiST content, the amount of the soluble fraction increases, allowing the crosslinked materials to soften due to the plasticizing effect of the oil rich phase and causing a sharpening of the tan δ peaks.

To determine the thermal stability and the decomposition behaviour of the copolymers, thermogravimetric analysis was carried out under nitrogen and air atmospheres. Figure 6 shows TGA curves and the first derivative curves

and table 3 summarizes TGA data. Under nitrogen atmosphere, samples were thermally stable below 300ºC and the degradation takes place in one step. No significant differences can be seen on $T_{10\%}$, T_{max} or R, indicating that all systems exhibit a quite similar thermal behaviour. In air, the copolymers are stable below 200ºC and a three stage weight loss can be seen at higher temperatures. The first stage is attributed to the decomposition of soluble components, while the second stage between 350 and 500ºC corresponds to the crosslinked polymer degradation that takes place at a faster rate. The thermooxidative degradation is observed at temperatures higher than 500ºC.

To test the flame retardancy of the copolymers, LOI measurements were carried out. LOI measures the ease of extinction of materials as the minimum percentage of oxygen in an oxygen/nitrogen atmosphere that will just sustain combustion in a candle-like configuration of a top-ignited vertical test specimen. LOI values increases from 19.2 for the silicon free system to 29.7 as the silicon content of the samples increases, so the presence of silicon improves the flame retardant properties of the copolymers.
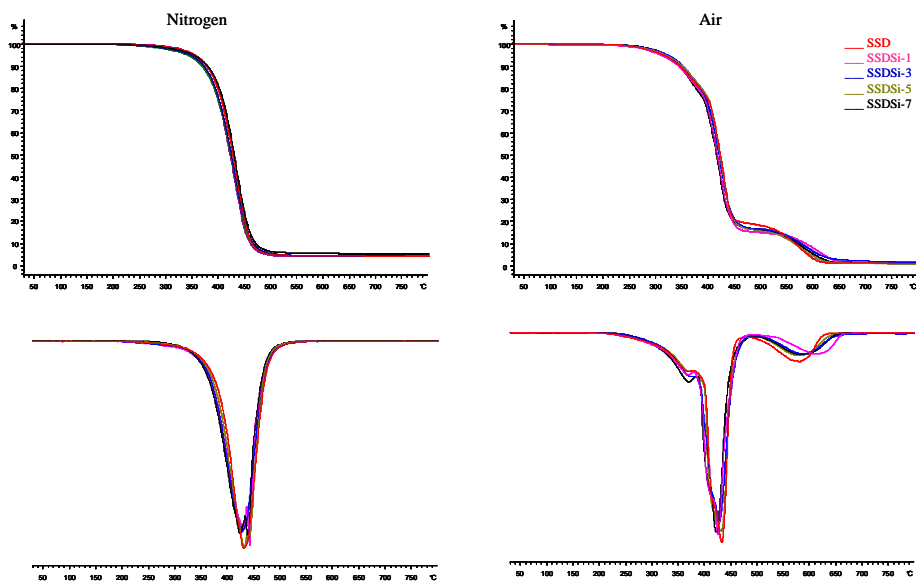
Figure 6. TGA plots (10ºC/min) and first derivative curves of the copolymers.

It is describe that Silicon-containing polymers can degrade forming thermally stable silica, which has the tendency to migrate to the char surface serving as a protection layer to prevent further degradation of char at high temperatures, leading to enhanced char formation at high temperatures. No significant differences can be observed among char yield for the different copolymers, thus indicating that the condensed flame retardant mechanism seems not to be responsible for the flame retardant improvement.

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CONCLUSIONS

Novel thermosetting copolymers have been prepared by cationic copolymerization of soybean oil, styrene, divinylbenzene and p-trimethylsilylstyrene (SiST) catalyzed by boron trifluoride diethyl etherate, with a silicon content between 1.0 to 7.0 wt% . The yield of the crosslinked polymer after soxhlet extraction decreases and the aromatic content of the soluble fraction increases with the amount of the SiST, according to the lower reactivity of this monomer. Dynamic mechanical analysis of the polymers indicates that the crosslinking density and the glass transition temperature decrease as the SiST amount increases. Thermogracimetric analysis shows that the presence of silicon does not change the thermal stability. The most notable change resulting from the incorporation of SiST is the increase of LOI values. Silicon containing copolymers no longer burn in ambient air without complementary oxygen, which suggest that these biobased materials are very interesting for applications that require fire resistance.

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2.2. Effects on the Flame Retardancy of Boron-Containing Soybean-Oil Based Copolymers

Effects on the Flame Retardancy of Boron-Containing Soybean-Oil Based Copolymers

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ABSTRACT

The first example of boron containing soybean oil based copolymers was prepared from soybean oil, styrene, divinylbenzene and 4-vinylphenyl boronic acid by cationic polymerization using boron trifluoride etherate as initiator. Soxhlet extraction and NMR spectroscopy indicate that the copolymers consist of a crosslinked network plasticized with varying amounts of oligomers and unreacted oil. Thermal, dynamomechanical and flame retardant properties of these materials were examined. Thermosets with glass transition temperatures ranging from 43 to 60ºC, which are thermally stable below 350ºC and with LOI values from 23.7 to 25.6 were obtained. The LOI tests indicate that the flame retardant properties of vegetable oil can be improved by adding boron covalently bonded to the polymer.

Keywords: vegetable oils, renewable resources, boron-containing polymers, flame retardancy

INTRODUCTION

The replacement of petroleum-based raw materials by renewable resources constitutes a major contemporary challenge in terms of both economical and environmental aspects.[1] Natural vegetable oils are considered to be one of the most important classes of renewable sources because of the wide variety of possibilities for chemical transformations, universal availability, and low price and they are preferred by the chemical industry as alternative.[2] Recently there have been many attempts to convert vegetable oils and fatty acids to useful polymers.[3] Vegetable oils such as soybean oil, sunflower oil or linseed oil are triglycerides of different fatty acids with varying degrees of unsaturation. It is generally considered difficult to polymerize vegetable oils themselves due to their lack of active functional groups. The thermal polymerization of vegetable oils at high temperature has been reported to give only low molecular weight polymers[4] and its cationic homopolymerization is relatively difficult.[5] Moreover the aliphatic nature and the light crosslinking that characterize the triglyceride-based materials make them incapable of displaying the necessary rigidity and strength required for structural applications by themselves. To overcome this drawback and improve the physical properties of solid thermoplastic and thermoset materials, the thermal or cationic copolymerization of natural oils with styrene and divinylbenzene or dicyclopentadiene[6] or from acrylated epoxidized natural oils and styrene have been proposed.[7]

Even though the resulting materials have the appropriate properties for a specific application, it must be inherently safe to be commercialized which involves to posses flame resistance and non toxic characteristics. Vegetable

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ISBN:978-84-693-1532-3/DL:T-649-2010

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oil-based materials, like many other organic polymeric materials, are inherently flammable and so the use of flame retardant additives or the copolymerization with flame retardant monomers are common strategies used in the industry to overcome this shortcoming. For decades, most of the organic flame retardants used in industry had been halogen-based compounds. However, the flame-retardant resins that contain halogens release hydrogen halides and dioxins during combustion, which causes corrosion and toxicity. The concept of sustainable development requires the development new environmentally friendly flame-retardant polymeric materials. Phosphorus, silicon and boron-containing polymers are well recognized for their flame retardant properties,[8] and they are increasingly becoming more popular than their halogen counterparts, as they generally give off nontoxic combustion products.[9] In spite of this, the preparation and characterization of vegetable oil-based materials incorporating these elements has been scarcely considered. In a previous work we described the preparation of styrene-soybean oil based copolymers containing silicon as effective environmentally friendly flame-retardant systems.[10]

Boric acid and borate salts have been used as flame retardant additives since the early 1800s but they have been studied less than phosphorus, silicon or other compounds specially in reactive systems.[11] The use of borates in enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century.[12] The flame retardant action of boron-containing compounds on polymeric materials is chemical as well as physical. Boron compounds thermally decompose producing boron oxide at the condensed phase and redirect the polymer decomposition process in favor of the char formation.[13] Char is a carbon-based soot/residue that undergoes very little oxidative

degradation, isolates the material from heat and flames and prevents the fuel molecules of being transported to the combustion surface. It is also postulated that the flame retardancy is related to the formation of an impenetrable surface layer of boron oxide ceramic or glass.[14] Furthermore, it may be possible for carbon-based char or boron carbide-type char to form under the glass layer. Like carbon char, this ceramic or glass provides thermal insulation and acts as a physical barrier to fuel transport. Primarily, the ceramic prevents heat from reaching the rest of the material, thus preventing melt, flow, and thermal decomposition.

Several strategies have been described to prepare reactive boron flame retardant polymers. The chemical modification of polymers, either by simple copolymerization with monomer containing boron groups or by post-polymerization modification,[15,16] enables flame retardance to be achieved often at much lower levels of modification than necessary with conventional additive-type compounds. Aromatic boronic acid based monomers are specially suitable because they are easy to synthesize and they are known to release water on thermolysis[17] which can improve the flame retardant behaviour by diluting the flammable volatile substances and providing a gas barrier to oxygen. In previous works we demonstrated that boronic acid containing styrenic monomers can be conveniently used to improve the flame retardance of styrenic polymers and thermosets.[18,19] Moreover the copolymerization of 4-vinylphenyl boronic acid with styrene-divinylbenzene mixtures and other unsaturated monomers have been well described.[20]

On the basis of these results and to further extend the use of renewable resources to obtain flame retardant polymers, we studied the preparation and

properties of boron containing soybean oil copolymers by cationic copolymerization of soybean oil, styrene and divinylbenzene with different amounts of 4-vinylphenyl boronic acid. The polymerization behaviour, structure, thermal stability and mechanical and flame retardant properties of the resulting materials have been investigated.

EXPERIMENTAL

Materials

Soybean oil (SOY) used in this study was supplied by Aldrich Chemical and has been used without further purification. It is primarily composed of unsaturated linoleic (C18:2), oleic (C18:1) and linolenic (C18:3) acids as well as saturated stearic (C18:0) and palmitic (C16:0) fatty acids. The content of other saturated and unsaturated fatty acids is negligible. ^{1}H NMR spectrum of soybean oil show signals at 5.4-5.2 ppm (characteristic of the olefinic hydrogens and the methine protons of the glycerin backbone), at 4.2-4.1 ppm (corresponding to the diastereotopic protons of the glycerin methylene units), at 2.7 ppm (corresponding to the methylene protons two C-C double bonds), at 2.3 ppm (assigned to the methylene protons adjacent to the carbonyl groups), and at 2.1 ppm (characteristic of the methylene protons adjacent to the C-C double bonds). The degree of unsaturation, expressed as the number of carbon-carbon double bonds per triglyceride, was 4.7 as obtained from the iodine index value and 4.5 from ^{1}H NMR spectroscopy (calculated from the area of the signal at 5.4-5.2 ppm and the area of the signal at 4.2-4.1 ppm).

Styrene (ST, 99.9%) and divinylbenzene (DVB, 80%) were purchased from Fluka and washed with a NaOH 10% solution and then with water. The distilled-grade boron trifluoride diethyl etherate ($BF_3.OEt_2$) used was supplied by Aldrich. Methyl oleate (MeOL, 75%) was purchased from Alfa Aesar. 4-bromostyrene, trimethylborate and butylithium (0.6M in hexane) were suplied by Aldrich and used as received. The solvents were purified using standard procedures.

4-Vinylphenyl boronic acid (VPB) was prepared from 4-bromostyrene and trimethylborate following a general reported procedure for boronic acid synthesis[21] and purified by crystallization in water. Yield: 61%, mp: 185-189ºC. Tris(4-vinylphenyl)boroxine (BST) was obtained by removing water azeotropycally with toluene following a reported procedure.[22] Yield: 92%, mp: 194-196ºC.

Cationic Copolymerization

The following reaction procedure was usually employed, unless otherwise stated in the text. The desired amounts of tris(4-vinylphenyl)boroxine, styrene and divinylbenzene were added to the soybean oil (Table 1). The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of a modified initiator (3 mol% of BF_3OEt_2 regarding to the total C=C double bond in the polymerization mixture). The modified initiator was prepared by mixing BF_3OEt_2 and MeOL in a molar ratio 1.1:1.0.

The reaction mixture was then injected into aluminium moulds and heated for 12h at the appropriate temperatures: at 60ºC for SSD, 70ºC for SSDB1

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and 90ºC for SSDB2 and SSDB3. In all cases, 24h of postcuring at 160ºC was applied.

Polymer Extraction

A 0.5 g sample of the bulk polymer was extracted for 24 h with 200 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation. The soluble and insoluble fractions were dried under vacuum for several hours before weighing and further characterization.

Characterization

The IR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in absorbance mode. An attenuated-total-reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra.

The ^{1}H and ^{11}B-NMR spectra were recorded at room temperature on a Varian Gemini 400-MHz spectrometer (400 MHz for ^{1}H and 96.3 MHz for ^{11}B) using TMS or BF_3OEt_2 as standards. For the monomers and copolymer soluble fractions $CDCl_3$ or $C_2D_2Cl_4$ (TCE-d_2) were used as solvents. Copolymer insoluble fractions were swollen in DMSO-d_6 or TCE-d_2. ^{1}H HR-MAS NMR spectra were recorded on a Brucker Avance III 500 spectrometer operating at a proton frequency of 500.13 MHz. The instrument was

equipped with a 4 mm triple resonance gradient HR-MAS probe. A Brucker Cooling Unit (BCU-Xtreme) was used to keep the sample temperature at 27ºC. Samples prepared with TCE-d_2 were spun at 6 kHz to keep the rotation side bands out of the spectral region of interest. One-dimensional ^{1}H NMR spectra were acquired in 1 min and 16 scans with a 1.0 s relaxation delay.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer with N_2 as the purge gas. The heating rate was 10ºC/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N_2 as the purge gas at scanning rates of 10°C/min. Boron content was determined by heating at 900ºC under air atmosphere for 5h. For each sample, three analyses were carried out. The percentage of boron was calculated from the weight of B_2O_3 measured after cooling the crucibles in a dry atmosphere.[23]

Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three point bending configuration. The various thermal transitions were studied between -100 and 100ºC at a heating rate of 3ºC/min and a fixed frequency of 1 Hz.

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RESULTS AND DISCUSSION

The cationic polymerization of soybean oil produces viscous oils due to the scarce reactivity of the internal double bonds. Moreover, boron trifluoride diethyl etherate as initiator has been found to be immiscible with the oil, thus the conversion to high molecular weight polymers has proven relatively difficult. The copolymerization of soybean oils, styrene and divinylbenzene using boron trifluoride diethyl etherate is also heterogeneous and completely homogeneous reaction media can be obtained when the initiator is modified with fish oil ethyl ester or soybean oil methyl esters.[5] In our case, the initiator system was obtained by mixing boron trifluoride diethyletherate with methyl oleate and homogeneous reactions were generated from a mixture of soybean oil, styrene and divinylbenzene in a molar ratio 1.00:6.00:2.25 (Sample SSD, Table 1). This ratio has been chosen because it affords the maximum oil incorporation into the polymer as described in the literature.[5] The amount of BF_3OEt_2 used was kept constant at 3 mol% regarding to the total C=C double bond in the polymerization mixture.

In a first instance 4-vinylphenyl boronic acid (VPB) was chosen as source of boron in the polymerization mixture. VPB acid was conveniently synthesized from 4-bromostyrene following a general procedure for aromatic boronic acids through the formation of the organolithium intermediate.[21] Attempts to polymerize mixtures of this boron-containing styrene monomer with different amounts of styrene, divinylbenzene and soybean oil were unsuccessful due to the poor solubility of the VPB in the polymerization mixture and in all cases heterogeneous materials were obtained.

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It is well known that boronic acids, specially the aromatic ones, undergo lost of water under very mild conditions leading to tris(aryl)boroxines.[24] This transformation can be completed by simply removing water by azeotropic distillation. The resulting product has a better solubility in most common solvents and thus it is expected to show higher solubility in the SOY/ST/DVB mixture (Scheme 1). In this way, we used this synthetic procedure to prepare tris(4-vinylphenyl)boroxine (BST) from VPB. The formation of the boroxine was confirmed by FTIR-ATR (disappearance of the broad band at ca. 3440 cm^{-1} of hydroxyl groups and the appearance of a band at 700 cm^{-1} characteristic of the boroxine ring),[25] and by ^{1}H NMR (absence of the signals corresponding to the hydroxyl groups at 7.2 ppm).

Soybean oil
(SOY)

Styrene
(ST)

Divinylbenzene
(DVB)

4-vinylphenyl boronic acid
(VPB)

tris(4-vinylphenyl)boroxine
(BST)
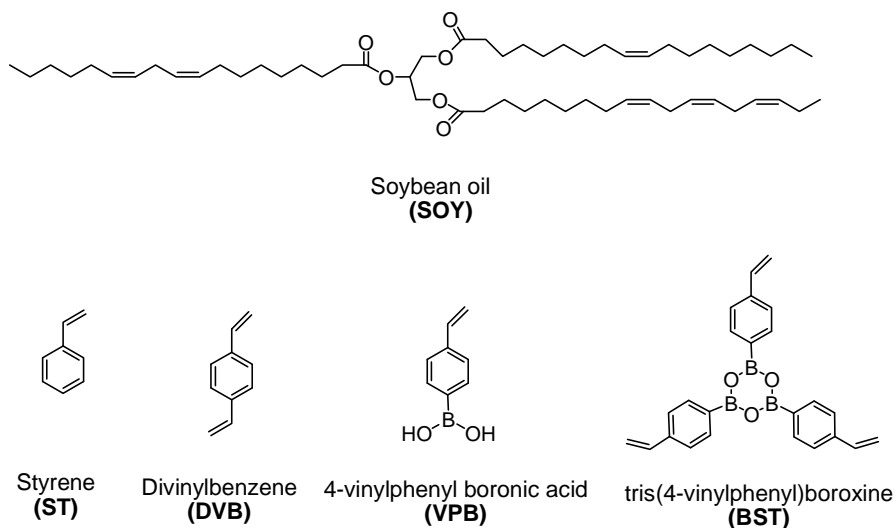
Scheme 1. Structure of the comonomers.

A set of four copolymerizations was carried out with compositions shown in Table 1. The first one, SSD, as above mentioned corresponds to a mixture of SOY/ST/DVB and was prepared for comparative purpose. The feed of the following copolymerizations was formulated by replacing part or the whole of ST by BST while the amount of DVB was kept constant. In this way, materials with 1%, 2% and 3% (w/w) of boron were obtained. The amount of catalyst (BF_3OEt_2/MeOL 1.1:1.0 mixture) was also kept constant to 3 mol % regarding to the total C=C double bond in the polymerization mixture.

Table 1. Molar composition, curing behaviour and curing conditions of the copolymerization mixtures (mols $BF_3.OEt_2$: 0.41).

Sample	%B	SOY	ST	BST	DVB	T_{onset}[a] ºC	T_{max}[b] ºC	Curing [c,d] T(ºC)
SSD	0	1.00	6.00	-	2.25	52	74	60
SSDB1	1	1.00	4.10	0.63	2.25	59	106	70
SSDB2	2	1.00	2.02	1.31	2.25	75	122	90
SSDB3	3	1.00	-	2.00	2.25	110	145	90

[a] Temperature of the onset of the crosslinking exotherm (10ºC/min).
[b] Temperature of the maximum of the crosslinking exotherm (10ºC/min).
[c] Curing for 12h.
[d] Post-curing at 160ºC for 24h.

Prior to the preparation of the thermosets, the curing reaction behaviour was studied by dynamic DSC (Figure 1 and Table 1) in order to establish the influence of the tris(4-vinylphenyl)boroxine in the polymerization mixture.

DSC plots show a broad exotherm that shifts to higher temperatures as the BST content increases. This seems to indicate a lower reactivity of the electron-poor vinyl groups in the boroxine. Moreover, the onset temperature of the curing exotherms increases progressively from 52ºC to 118ºC. According to these results different curing treatments were applied for each sample. Moreover, different curing times and post-curing temperatures were tested in order to achieve the maximum extent of the copolymerization. In this way, 12h for the curing process and 24h at 160ºC for the post-curing one were selected. Higher temperatures or longer times did not increase the crosslinked fraction in a significant way.
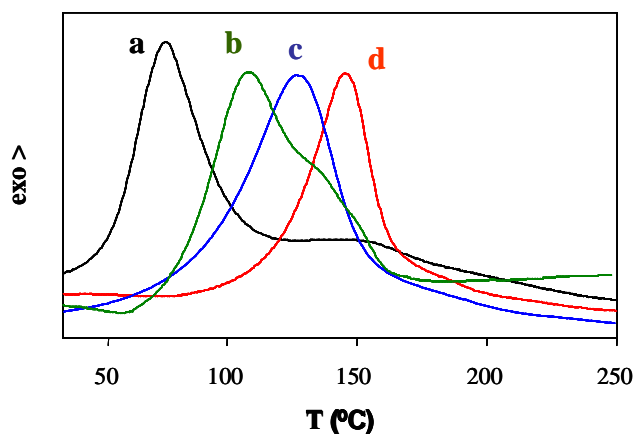
Figure 1. DSC plots (10ºC/min) of curing mixtures (a) SSD, (b) SSDB1, (c) SSDB2 and (d) SSDB3.

The fully cured soybean oil copolymers have been obtained in essentially quantitative yields. All the copolymers appear as brown tough and ductile

rubbers at room temperature. FTIR analyses have been performed to characterize the resulting materials. Bands at 1739, 1600 and 1452 cm^{-1} confirm the presence of the triglyceride carbonyl groups and aromatic moieties, respectively.

The existence of unreacted C=C bonds is not clear as the expected weak band at 1652 cm^{-1} overlaps with the broad intense signals of the ester groups and the aromatic rings. For the boron-containing copolymers, the most significant trend is the presence of the B-O stretching band at 1350 cm^{-1} and of a broad band at ca. 3300 cm^{-1} corresponding to boronic hydroxyl groups. This band indicates that in spite of using the boroxine as starting monomer, eventually the boronic acid is obtained in the cured material. The presence of traces of remaining boroxine units could not be confirmed as their characteristic band at 680-700 cm^{-1} overlaps with the strong band at 698 cm^{-1} corresponding to the phenyl ring out of plane deformation characteristic of the styrenic moieties.

The composition of these copolymers and their characterization has been also considered. The results of this analysis are summarized in Table 2. To measure the amount of crosslinked and uncrosslinked fraction, Soxhlet extraction with methylene chloride was used. Typically after 24h extraction, 73-92 wt % of insoluble fractions are retained from the bulk materials. The yield of the insoluble material from the SSDB1, SSDB2 and SSDB3 systems is comparable but noticeably lower than that of the SSD system, probably because of the lower reactivity of BST.

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Table 2. Composition of the copolymers.

Sample	Feed composition (w%)		Soluble fraction		Insoluble fraction		
	B (w %)	Aromatic fraction	Yield (w %)[a]	Aromatic frac. (%)[b]	Yield (w %)[a]	B (%)[c]	Aromatic frac. (%)[d]
SSD	-	47	8	13 (2)	92	-	50 (98)
SSDB1	1	49	25	15 (8)	75	1.1	60 (92)
SSDB2	2	51	25	20 (10)	75	2.3	61 (90)
SSDB3	3	53	27	25 (12)	73	3.6	63 (88)

[a] Weight percent of the soluble and insoluble fractions after Soxhlet extraction with methylene chloride.
[b] Weight percent of the aromatic components in the soluble extracts calculated from the ^{1}H NMR spectra. Values in brackets correspond to the percentage of the aromatic feed incorporated in the soluble fraction calculated indirectly.
[c] Calculated from the B_2O_3 residue after pyrolysis at 900ºC under oxygen atmosphere.
[d] Weight percent of the aromatic components in the insoluble fraction. Values in brackets correspond to the percentage of the aromatic feed incorporated in the insoluble fraction. All values are calculated indirectly from the percentages of the soluble fraction.

The soluble fractions were characterized by ^{1}H NMR spectroscopy (SSD3, Figure 2c) and from the peak areas of the aromatic protons signal (broad signal centered at 7.0 ppm) and the glycerine methylene protons (4.2 ppm), it is possible to calculate the molar ratio of the aromatic and oil components present in the soluble extracts and the percentage of the feed aromatic content that is incorporated in the soluble fractions. Data for the insoluble fractions can be calculated indirectly from these values and results are collected in table 2. Moreover, the boron content of the insoluble fractions was determined from the B_2O_3 residue at 900ºC by thermogravimetric analysis.

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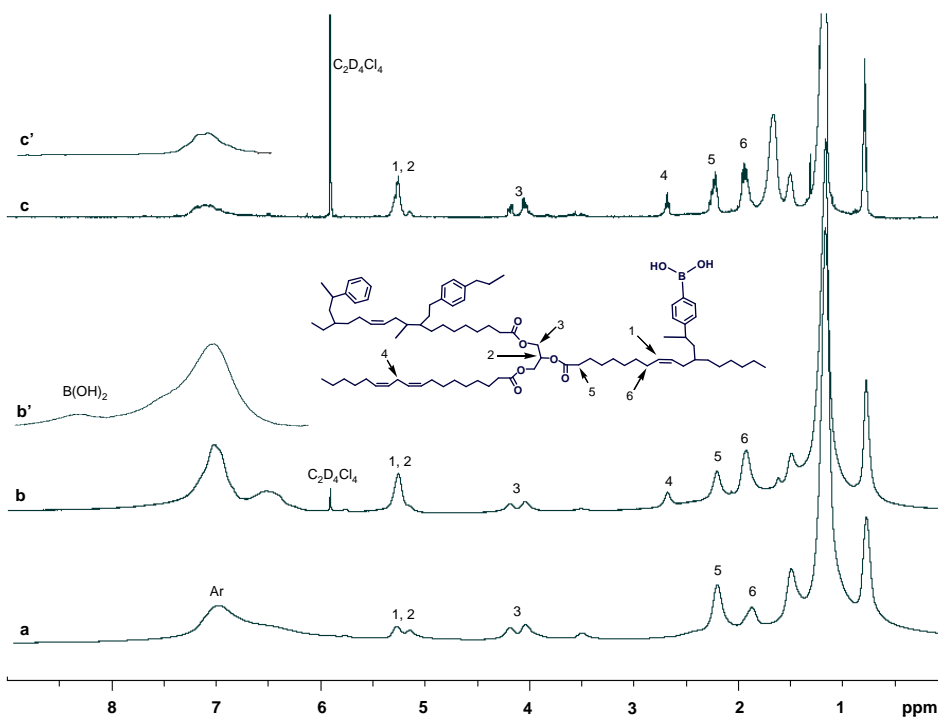
Figure 2. ^{1}H HR-MAS NMR spectra of the insoluble fractions of samples SSD (a) and SSDB3 (b) swollen in TCE-d_2 and b') SSDB3 swollen in DMSO-d_6. ^{1}H NMR spectra of the soluble SSDB3 fraction recorded in TCE-d_2 (c) and in DMSO-d_6 (c').

As can be seen in Table 2, the boron percentage and the aromatic fraction content of the insoluble fractions is higher than the expected from the feed which indicates that aromatic monomers are mostly incorporated in the crosslinked fraction and confirms that the soluble fractions are composed mainly by soybean oligomers. High Resolution MAS NMR spectroscopy was used as a useful tool to further study the extent of the crosslinking reaction in the insoluble fractions. Conventional solid NMR spectroscopy usually results in signal broadening due to the lack of molecular mobility. However, HR-

MAS NMR spectroscopy reduces significantly this broadening by spinning the sample around an axis oriented at an angle $\theta = 54.7°$ with the direction of the magnetic field. The sample is spinned at a rate larger than the anisotropic interactions causing them to be averaged to their isotropic value and therefore, resulting in signal narrowing. To obtain a good spectrum, a solvent must be added that swells the polymer to some extent. However, the swelling is less effective in the sections of the polymer with a higher crosslinking density. As a result, crosslinking sites cannot be seen with the same resolution as the sections with higher mobility. Figure 2 depicts the ^{1}H HR-MAS NMR spectra of the insoluble fractions of samples SSD (a) and SSDB3 (b) swollen in TCE-d$_2$. In the same figure the ^{1}H NMR spectra of the soluble SSDB3 (c) fraction recorded in TCE-d$_2$ and the aromatic region of the insoluble and soluble SSDB3 (b' and c') fractions recorded in DMSO-d$_6$ are included for comparative purpose. The spectrum of the insoluble SSD shows a broad signal at 7.4-6.2 ppm corresponding to the aromatic protons of the ST and DVB, a signal at 5.5-5.2 ppm, attributed to the vinylic protons and glycerol methine protons of the soybean units, and a doublet at 4.3-4.0 ppm, corresponding to the glycerol methylene protons of the soybean. The small signal at about 3.5 ppm (-OCH$_3$) confirms the presence of methyl oleate as part of the initiator system. The signal at 2.3 ppm corresponds to the methylene directly attached to the ester group. Moreover, signals attributed to the methylene protons adjacent to the C=C bonds of the soybean oil can be seen at 1.9 ppm, according to the existence of unreacted moieties. The most significative difference when comparing to the boron-containing insoluble SSD3 sample is the small peak at 2.7 ppm that corresponds to the methylenes adjacent to two C=C bonds in the soybean oil. The fact that this peak cannot

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be observed in the SSD copolymer and that the intensity of peak at 1.9 ppm is lower, suggests a higher degree of polymerization of the soybean double bonds in the boron free polymer. This trend seems to confirm the higher reactivity of the boron-free system which is in agreement with the high yield of the insoluble fraction.

The ^{1}H NMR spectra of all soluble fractions resulted similar and show the same signals observed in the insoluble fractions but with a relative lower intensity of the aromatic region. In any case, unreacted monomer could be detected as can be seen in the representative spectrum of the soluble SSDB3 fraction (Figure 2c). To refine the structural analysis and to detect signals attributable to the boron moieties we recorded the spectra of the soluble and insoluble fractions in DMSO-d_6. The aromatic zone of the spectrum of the boron-containing insoluble fractions (Figure 2b') shows a small intensity peak at 8.4 ppm, in addition to the broad peak corresponding to the aromatic protons at 6.0-7.2 ppm. This peak, which appears in the spectrum of VPB recorded in DMSO-d_6, can be attributed to the boronic hydroxyl groups. The presence of this peak confirms that boron is in the boronic form and seems to indicate that the boroxine ring could open after the curing process. Interestingly, when the same spectra region of the boron-containing soluble fractions was analyzed, no hydroxylic protons were detected even in the soluble SSDB3 sample (Figure 2c').

DMA has been used to investigate the dynamic mechanical behavior of the copolymers. Figure 3 shows the storage moduli and the tan δ values of the samples with different boron content. At temperatures below -40ºC the copolymers are in the glassy state and their storage moduli decrease slightly

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with increasing temperature. A rapid decrease in the E' value of roughly 4 orders of magnitude is observed in the temperature range from –30 to 100 ºC, corresponding to the primary relaxation process of the copolymers. The energy dissipation associated to the modulus decrease can be seen as a maximum in the tan δ versus T curve. The modulus reaches a plateau at higher temperatures which is assigned to the rubbery state. The presence of the rubbery plateau in the DMA curve is evidence for the existence of a stable crosslinked network and according to the kinetic theory of rubber elasticity, the crosslinking density of the copolymer γ can be determined from the rubbery moduli using the following equation

$$E' = 3\gamma RT$$

where E' is the storage modulus of the crosslinked copolymer in the rubbery region above the glass transition temperature, R is the universal gas constant and T is the absolute temperature. Rubber elasticity theory is not expected to completely apply to the highly crosslinked polymers, but should show general trends in how crosslinking density is affected by the BST content. The values of the storage moduli E' used for calculations were taken 50ºC above the Tg and are collected in Table 3. The crosslinking density of the boron free sample, 6.6×10^2 mol/m^3, is in the range of the previously described SSD copolymers.[26] It is much higher than those of the boron-containing samples. Since the storage modulus is a manifestation of the crosslinking density and hence of the network stiffness, this can be attributed to the higher soluble fraction present in these copolymers.

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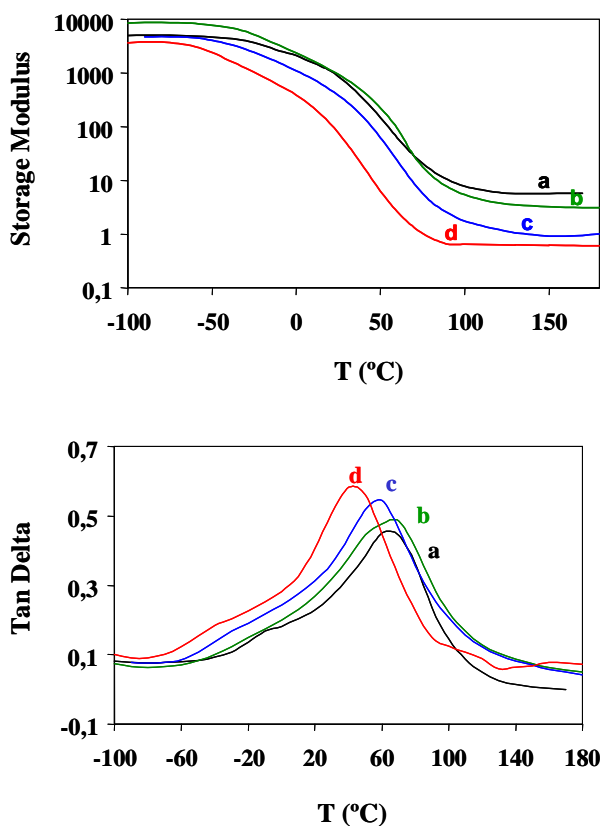
Figure 3. Storage modulus and loss factor of the copolymers.

Moreover, it decreases with the increase in BST content, in spite of the similar soluble fraction percentage of these materials. This fact should be related to the opening of boroxine ring and the presence of free VPB units, which would significantly decrease the crosslinking density

From the tan δ plots of Figure 3, a shoulder at low temperatures can be observed indicating the existence of two glass transition temperatures which merge into a very broad transition. This seems to confirm that the obtained

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copolymers are complex heterogeneous systems composed of hard aromatic rich domains and soft oil rich domains, in addition to some amount of oligomers which act as plasticizers.

Table 3. Thermal properties of the copolymers.

Sample	ν_e (mol/m^3)[a]	Tg (ºC)[b]	Nitrogen			Air			LOI
			$T_{10\%}$ (ºC)[c]	T_{max} (ºC)[d]	Yield 800ºC (%)[e]	$T_{10\%}$ (ºC)[c]	T_{max} (ºC)[d]	Yield 800ºC (%)[e]	
SSD	659	62	378	432	4.7	349	362, 434, 582	0.6	19.2
SSDB1	417	60	357	421	6.2	351	360, 425, 584	5.2	23.7
SSDB2	155	51	355	428	13.2	344	362, 430, 576	10.1	24.6
SSDB3	70	43	359	435	15.9	332	365, 436, 560	13.7	25.6

[a] Crosslinking densities calculated 50ºC above the corresponding Tg .
[b] Glass transition temperatures calculated from the maxima of the Tan δ curves.
[c] Temperature of 10% weight loss.
[d] Temperature of the maximum weight loss rate.
[e] Char yield at 800ºC.

The high temperature transitions (62º to 43ºC), correspond to the glass transition temperatures of the plasticized aromatic rich phases, while the low temperature transitions (-10ºC to -41ºC) are attributed to the oil rich phases.

The shift of the higher Tg to lower temperatures with the increase in the BST content seems to indicate that the crosslinked polymer becomes more compatible with the oil rich phase and is in accordance to the presence of free VPB units above mentioned. As expected, the height of the tan δ peaks

increases as the amount of BST increases confirming the lower crosslinking density and the higher segmental mobility.

To determine the thermal stability and decomposition behaviour of the copolymers, thermogravimetric analysis was carried out under nitrogen and air atmospheres. Figure 4 shows TGA curves and the first derivative curves and Table 3 summarizes TGA data. Under both nitrogen and air atmosphere, samples were thermally stable below 300ºC but a slight drifting starting around 100ºC can be observed. This weight lost becomes more important as the temperature and the BST content increase and can be attributed to the dehydration reaction leading to boroxine rings when higher temperatures are reached.[23] Under nitrogen atmosphere only one degradation step is observed independently of the polymer composition. No significant differences can be seen on $T_{10\%,}$ T_{max} or char yield at 800ºC, indicating that all systems exhibit quite similar thermal behaviour. In air, three weight loss stages can be seen. The first stage around 360ºC can be due to decomposition of soluble components, while the second stage around 400-450ºC corresponds to the crosslinked polymer degradation that takes place at a faster rate. The third stage is observed at temperatures around 600ºC and corresponds to the thermooxidative degradation.

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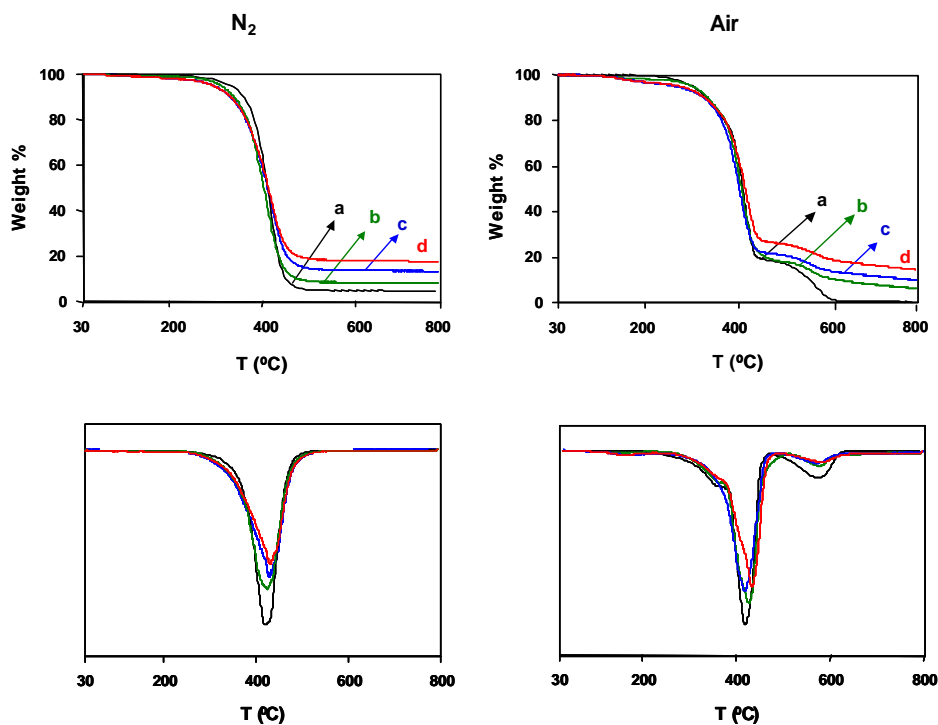
Figure 4. TGA plots (10ºC/min) and first derivative curves of the copolymers.

The rate of this stage decreases as the percentage of BST increases. Moreover, while the char yield for the SSD is practically non-existent, the char yields for the boron containing resins increase with the boron content (Table 3). The boron, therefore, plays a role in char formation and because char yield has been correlated to flame retardancy,[27] these polymers were expected to have good flame-retardant properties.

To test the flame retardancy of the copolymers, LOI measurements were carried out. LOI measures the ease of extinction of materials as the minimum percentage of oxygen in an oxygen/nitrogen atmosphere that will just sustain

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combustion in a candle-like configuration of a top-ignited vertical test specimen. LOI values increase from 19.2 for the boron free system to 23.7 for the resin with the lowest boron content (1% B). As the boron content increases, the LOI value goes up to 25.6. It has been described[15,18] for boron-containing linear styrenic polymers that boron contents higher that 3% are needed to get small increases in the LOI values. Previous work on silicon-containing soybean oil copolymers showed similar LOI values for similar heteroatom percentages.[10] Our results show that when boron is chemically attached to the network significant LOI increases can be obtained even when using 50% of renewable materials of aliphatic structure.

CONCLUSIONS

Novel thermosetting copolymers have been prepared by cationic copolymerization of soybean oil, styrene, divinylbenzene and tris(4-vinylphenyl)boroxine (BST) catalyzed by boron trifluoride diethyl etherate, with a boron content between 1.0 to 3.0 wt%. The yield of the crosslinked polymer after soxhlet extraction decreases in presence of BST. Dynamic mechanical analysis of the polymers indicates that the crosslinking density and the glass transition temperature decrease as the BST amount increases. Thermogravimetric analysis shows that for boron-containing copolymers dehydratation processes occur when heating, strengthening the network by the formation of boroxine rings. The presence of boron does not change the thermal stability. The incorporation of BST into the polymer matrix results in a notable increase of LOI values. Boron-containing copolymers no longer

burn in ambient air without complementary oxygen, which suggest that these

biobased materials are interesting for applications that require fire resistance.

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2.3. Cone Calorimetry Studies of Fire Retardant Soybean-Oil-Based Copolymers Containing Silicon or Boron: Comparison of Additive and Reactive Approaches

Cone Calorimetry Studies of Fire Retardant Soybean-Oil-Based Copolymers Containing Silicon or Boron: Comparison of Additive and Reactive Approaches

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ABSTRACT

The fire retardance and thermal stability of soybean-based copolymers reactively modified by copolymerization with trimethylsilylstyrene (SiST) and tris-(4-vinylphenylboroxine) (BST) have been compared with those prepared with equivalent amounts of the additive 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (SiAD) and tris-(phenylboroxine) (BAD) and with the heteroatom free soybean based copolymers. The best results are obtained for the boron containing copolymers. The reactive or additive approach is a significant factor in terms of the level of fire retardance achieved.

INTRODUCTION

Biomaterials, chemicals, and energy from renewable resources have received considerable interest in recent years.[1] The advantages of using renewable feedstocks in polymer synthesis such as vegetable oils include their low cost, ready availability, and sustainability, as well as possibly enhanced compostability and biodegradability of the resultant polymer materials at their end of life.

Vegetable oils containing unsaturated fatty acids can be used in polymerizations to make biobased polymers.[2-5] However, in common with other aliphatic polymer materials they are highly combustible. The concept of sustainable development requires technologies to be developed which have minimum impact on health and the environment through the life cycle of the material; that is to say, its synthesis, fabrication, use, recycling and disposal. Since most synthetic materials cause disposal problems after use and unwanted fires cause major environmental damage, as well as wasting resources, it is essential that sustainable strategies for fire retardant materials are developed. The incorporation of silicon or boron functionality in the polymeric structure is recognized as one of the most efficient ways to obtain an environmentally friendly fire-retardant system.[6]

Generally, fire retardancy is achieved by the physical incorporation of additives; however, this method has several disadvantages.[7] For example, halogen based flame-retardant additives may be leached from the polymer to the environment, where they have been shown to act as endocrine disruptors. They also have to be used in significantly high concentrations in order to be effective, which may adversely affect the physical and mechanical properties

of the material. The alternative strategy of using reactive flame retardants may be achieved by copolymerization with comonomers containing fire retardant groups. The relatively low loadings required to reduce the flammability do not produce significant changes in physical and mechanical properties of the polymer. Furthermore, the fire retardant chemical is then permanently attached to the polymer. This latter method is the focus of our study.

We have obtained fire retardant silicon-[8] or boron-containing[9] polymers by copolymerization of soybean oil and styrenic monomers containing covalently bonded silicon or boron. We have concentrated on the use of silicon and boron containing species as reactive modifiers as they have been investigated less than phosphorus species. Silicon compounds, when present in a polymer, have a fire retardant effect arising partly from vapour phase action, dilution of combustible organic gases in the flame zone, and partly from the formation of a barrier to heat and mass transfer that silicaceous residues can form behind the flame front.[10,11] Boron compounds thermally decompose producing boron oxide in the condensed phase and alter the decomposition process of the polymer in favour of carbonaceous residues rather than CO or CO_2.[12,13] The aim of the present work is to explore the influence of these heteroatoms on the thermal and fire retardant properties of soybean oil-based copolymers, and to compare the combustion behaviour of silicon- or boron-containing polymers obtained by copolymerization with Si- or B-containing reactive fire retardants or by adding Si- or B-containing fire retardants additives (Scheme 1).

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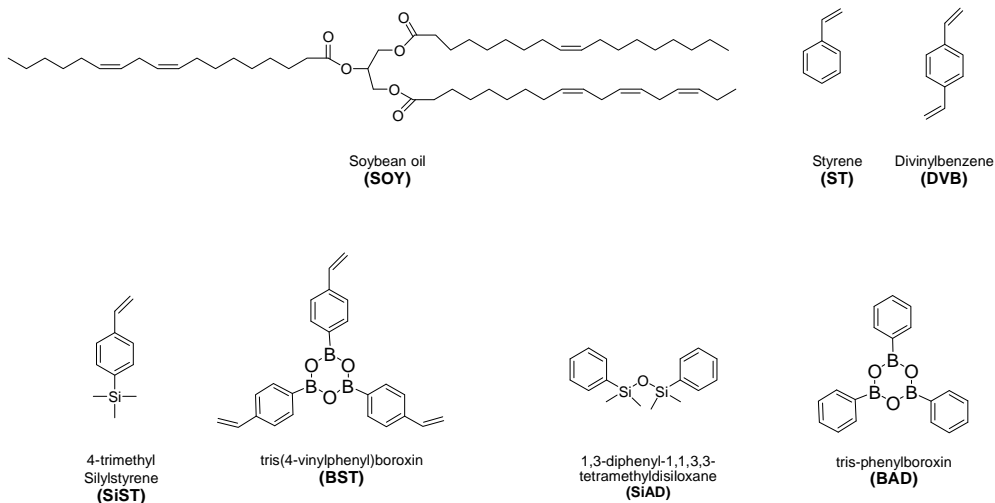
Scheme 1. Structures and identities of the additives and comonomers.

Flammability is a complex scenario dependant phenomenon which cannot be represented by a single numerical quantity. Ignitability indicates proper sites for a fire to start, or for flame spread, and is often measured by easy of extinction tests such as the Limiting Oxygen Index (LOI, ISO 4589).[14] Cone calorimetry (ISO 5660)[15] gives a more complete picture of burning behaviour, particularly looking at spark piloted face ignition (using the retaining frame) with the sample in a horizontal orientation. Interpretation of cone calorimetry data for development of fire retarded materials has been discussed elsewhere.[16]

EXPERIMENTAL

Materials

Soybean oil used in this study (iodine value = 135) was supplied by Aldrich Chemicals and has been used without further purification. Styrene (ST, 99.9%) and divinylbenzene (DVB, 80%) were purchased from Fluka and washed with a NaOH 10% solution and then with water. The distilled-grade boron trifluoride diethyl etherate ($BF_3.OEt_2$) (Aldrich), methyl oleate (MeOL, 75%) (Alfa Aesar), 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (SiAD) (ABCR) and tris-(phenylboroxine) (BAD) (Aldrich) were used without further modification. 4-trimethylsilylstyrene[8] and tris(4-vinylphenyl)boroxine[9] were obtained as previously described.

Synthesis of polymer plaques

The desired amounts of comonomers or additives were added to the soybean oil (Table 1). The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of a modified initiator (in a 3 mol% of BF_3OEt_2 ratio to the total C=C double bond in the polymerization mixture). The modified initiator was prepared by mixing BF_3OEt_2 and MeOL in a molar ratio 1.1:1.0. Plaques of the different copolymers for cone calorimetric experiments were prepared by mixing the different components. The mixtures were placed in a 100 x 100 x 2,0 mm^3 aluminium moulds. Curing conditions are shown in Table1.

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LOI measurements (LOI ISO 4589)[14]

These were performed on a Stanton Redcroft FTA flammability unit provided with an Oxygen Analyzer. Sample sizes measured 100 x 5 x 4mm^3 and were prepared by moulding.

Thermogravimetric analysis (TGA)

Dynamic thermogravimetric studies were used to investigate the behaviour in an oxidative and non-oxidative environment using a Mettler TGA/SDTA851e/LF/1100 instrument. For both air and nitrogen atmospheres a flow rate of 10 ml/min was used. Samples of 10-15 mg were placed in open alumina pans and heated from 30 to 800 ºC at a constant heating rate of 10 ºC/min.

Cone calorimetry

The combustion behaviour of the polymer plaques, 100 x 100 x 2 mm, was investigated using a Fire Testing Technology cone calorimeter in following ISO 5660[15], at a heat flux of 35 KW m^{-2}, which is the recommended heat flux for exploratory testing.[17] The plaques were placed in the sample holder with a retainer frame, resulting in 88 cm^2 of the sample surface being exposed to the radiation from the cone heater. Due to the processes involved in sample preparation each test was only carried out twice, giving an indication of the reproducibility of the results. Averages of the two values are presented in the results.

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Dynamic mechanical thermal analysis (DMTA)

Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three point bending configuration. The various thermal transitions were studied between -100 and 100ºC at a heating rate of 3ºC/min and a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Combustion behaviour

Soybean oil based copolymers containing silicon or boron covalently attached to the network and containing silicon or boron additives have been obtained with the compositions and curing conditions shown in Table 1.

The easy of extinction of these systems have been assessed by the LOI test and the results are given in Table 2. The LOI value of the heteroatom free soybean oil-based copolymer is 19.2 and increases significantly when silicon or boron, either in additive or reactive form, are added, indicating a reduction in ignitability. No significant differences are observed from the reactive and additive approach for a 3% B content and only a small improvement is observed for a covalently bonded silicon containing copolymer (CSiR) compared to the silicon additive approach (CSiA).

Table 1. Molar ratio of the different copolymers synthesized (DVB:2.25, MeOL:0.36; BF_3OEt_2: 0.41) and curing conditions.

System	SOY	ST	SiST	SiAD	BST	BAD	%Si	%B	t(h)	T(ºC)	t(h)	T(ºC)
				Molar ratio and Si and B content						Curing conditions		
C	1	6	-	-	-	-	-	-	12	60	24	110
CSiR	1	2	4	-	-	-	5	-	12	60	24	140
CSiA	1	6	-	2.3	-	-	5	-	12	90	24	160
CBR	1	0	-	-	6	-	-	3	12	90	24	160
CBA	1	6	-	-	-	8.1	-	3	12	120	24	160

Whilst measurement of LOI is a useful, small-scale test that correlates to the ignitability in polymers, it is not a reliable indicator of how a material will perform once ignited in a real fire. The most widely used method for this is the cone calorimeter, in which a polymer plaque is irradiated at a pre-determined heat flux, simulating the conditions of an advancing flame front. Some important parameters obtained for plaques of the different soybean-based copolymers prepared are given in Table 2.

Ignition occurs when the mass loss rate produces sufficient volatiles with an effective heat of combustion capable of sustaining ignition piloted by a spark. The heteroatom containing samples have improved times to TTI, except for the CSiA system.

While for the boron containing copolymers, the presence of the heteroelement seems to be a significant factor in the ignition time, for the silicon containing copolymers not only the presence of silicon but also the reactive nature of the fire retardant appears to be important. This could

indicate an early decomposition of SiAD before it could play a role as a fire retardant.

Table 2. LOI and cone calorimetric data measured with an irradiance of 35 KW/m^2.

Sample	LOI	TTI (s)	HRR$_{peak}$ (KW/m^2)	THR (MJ/m^2)	FIGRA (KW/m^{2}s)	MARHE (KW/m^2)	Total Smoke Release (KW/m^2)
C	19.2	25	509	36.7	7.3	235	742
CSiR	28.6	37	616	43.8	8.8	244	1189
CSiA	26.0	18	928	33.7	18.5	412	1402
CBR	25.6	44	409	32.5	3.7	178	371
CBA	15.2	52	527	32.8	6.6	278	986

The heat release rates (HRR) vs. time curves for the copolymers are presented in Figure 1. The HRR of C increased rapidly after the initial 25 s and the peak heat release rate (PHRR) occurred at 70 s. Subsequently, the HRR decreased rapidly until it became negligible after 300s. The shape of HRR curves is similar for all the copolymers. The results show a significant decrease of 20% on the value of PHRR for the CBR system, while the system with a similar boron content as a flame retardant additive show a similar value. For the silicon containing copolymers, increases on the PHRR can be observed, especially important for the CSiA system. The values of the total heat evolved are very similar for all the samples. Unlike the time to ignition, the heat release rate and the total heat evolved do not correspond to LOI results illustrating the difference of these parameters in fire retardancy studies.

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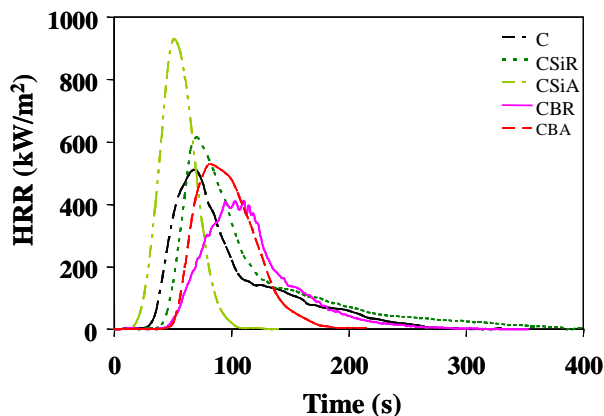
Figure 1. HRR vs. time for the different copolymers synthesised.

The Fire growth rate index (FIGRA) is calculated by dividing the peak heat release rate by time to peak heat release rate, and can estimate both the predicted fire spread rate and the size of a fire. The FIGRA index clearly diminishes for the boron reactive flame retardant containing copolymer, giving comparable values for CBA and CSiR and a twofold value for CSiA.

The average rate of heat emission (ARHE) curve is reported in Figure 2. This parameter, defined as the cumulative heat emission divided by time and its peak value (Maximum average rate of heat emission, MARHE) can be considered a good measure of the propensity for fire development under real scale conditions. MARHE for CBR system shows a notable reduction (24%) with respect to the C sample, while the incorporation of boron in additive form or silicon in reactive form show slight increases. The CSiA system, however, shows an increase of about 60%.
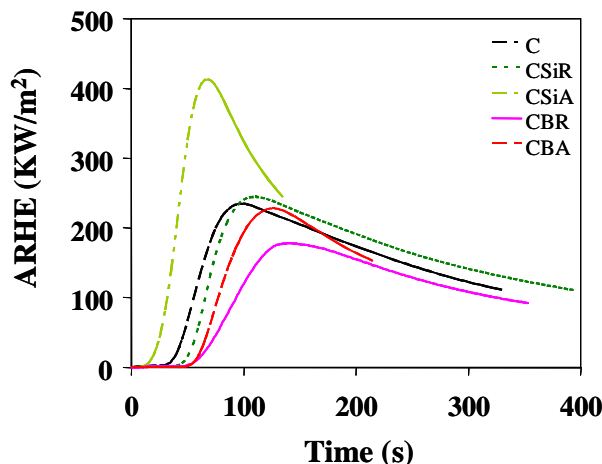
Figure 2. ARHE vs. Time for the different systems.

Mass loss vs. time

Percentage mass loss curves obtained as a function of time for the copolymer and additive systems are presented in Figure 3. The residual mass shown for the C, CSiR and CSiA systems is negligible. Conversely, the boron-containing copolymers (as reactive or additive fire retardants) showed a residual mass above 10% at the end of the tests. The observance of char seen during the cone calorimetry testing of CBR and CBA suggests a condensed-phase mechanism of fire retardancy. When these copolymers begin to burn and decompose, the boron oxide glass/boroxine networks, or organoceramic layers may act as a barrier to fuel transport and reradiate the incident flux from the cone calorimeter heater. Specifically, they are slowing the release of fuel from the decomposing polymer to the flame front.

Furthermore, the char formation may occur through prevention of fuel flow to the flame front. Small molecules and decomposition products containing free radicals now have longer residence times in the condensed phase and, as such, are more likely to form char.[18-22]
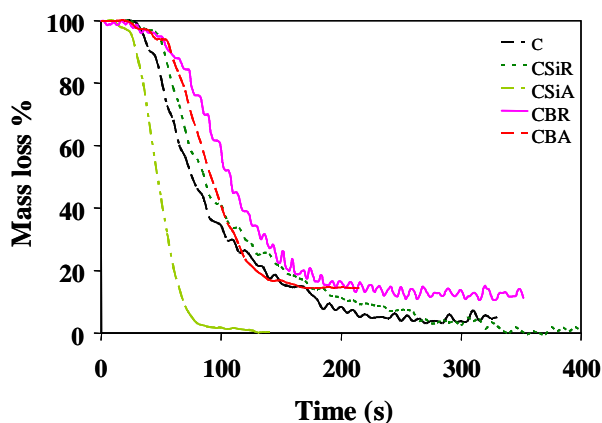
Figure 3. Mass loss curves (%) vs. Time for the different samples.

The values of the residual mass after combustion in cone calorimetry correlate well with the improvement in the peak heat release rate determined by cone calorimetry, according to a fire retardant mechanism being related to the formation of a char layer, except for CBA.

The thermal stability and decomposition behaviour of the copolymers were investigated by thermogravimetric analysis (TGA). Figure 4 presents the TGA curves of the copolymers in air and in N_2, and the thermogravimetric data are given in Table 3. When comparing char yields in nitrogen and air

atmospheres obtained by TGA with the residual masses after combustion in cone calorimetry a good correlation can be observed, showing a close relationship between the cone calorimeter and TGA char yields in nitrogen atmosphere that highlights the anaerobic environment under a flame during combustion and the role of char formation in improving fire performance.[23]
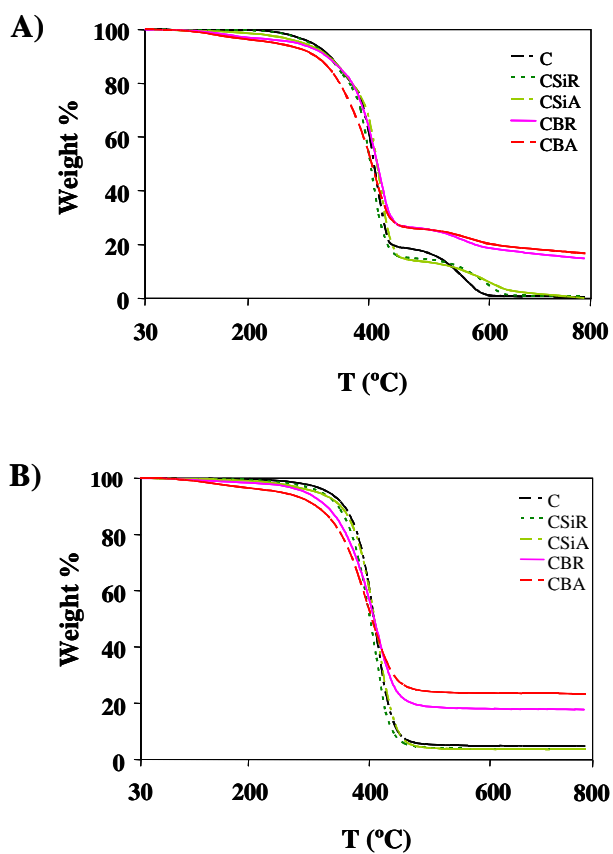
Figure 4. TGA plots **A)** under air and **B)** under nitrogen of the cured systems.

Table 3. Residue from cone calorimeter and thermogravimetric tests.

Sample	Cone calorimeter (%)	TGA Nitrogen		TGA Air	
		$T_{5\%}^{a}$ (ºC)	Char^{b} (%)	$T_{5\%}^{a}$ (ºC)	Char^{b} (%)
C	4.0	349	4.7	317	0.6
CSiR	0.7	340	3.8	310	0.9
CSiA	0.2	330	3.5	301	0
CBR	10.9	311	15.9	290	13.7
CBA	14.4	269	23.3	251	16.6

a Temperature of 5% weight loss.

b Char yield at 800ºC.

As can be seen, the presence of silicon covalently bonded to the polymer does not significantly change the thermal stability of the material. The polymer containing reactive boron fire retardant shows much lower thermal stability. For CBA, the weight loss at low temperatures has been attributed to the dehydration reaction of boronic acid groups that can be formed by partial opening of the boroxine rings after the curing process. The temperatures at which the additive containing polymers begin to degrade are lower than the corresponding reactive fire retardant containing polymers, a consequence of the volatilization of SiAD and BAD. No differences can be observed on the shape of the reactive and additive-containing polymers for each heteroatom, according to the degradation behaviour previously described for these copolymers.[8,9]

The shape of the weight loss curves obtained from the cone calorimeter test are similar to those obtained from thermogravimetry in nitrogen, but show differences with those obtained from thermogravimetry in air. On heating in a thermobalance at 10ºC/min in air, our systems show a two-step weight loss corresponding to two different degradation mechanisms (decomposition of soluble polymer fractions and degradation of the crosslinked network)[8,9] whereas a single step is observed during the combustion test. This can be due to the different heating conditions during the cone calorimeter test where a high heating rate and a high temperature are reached.

Smoke and CO evolution

Due to the presence of aromatic structures, burning these systems evolves large amounts of smoke that is known to be hazardous in fire situations. Only the sample containing the reactive boron fire retardant shows a significant decrease in the amount of smoke evolved, thus showing that the incorporation of boron covalently bonded to the copolymer reduces the smoke hazard compared to the soybean oil copolymer. The amounts of smoke evolved in our cone experiments were consistently higher for the samples containing additive fire retardants than reactive fire retardants.

The temporal behaviour of CO evolution rate during the cone calorimetry experiments is shown in Figure 5. As can be seen, the fire-retardant strategy applied, i.e. additive vs. reactive approach, did not significantly influence the amounts of CO evolved during combustion which generally follows the heat release curve. Both CO and smoke production indicate the fire retardancy

mechanism. Flame inhibition results in an increase in combustion products typical for incomplete combustion, with corresponding increases in CO and smoke production whereas increased charring shows no change or even a reduction in the absolute CO production due to an unchanged yield (based on mass lost and a reduced total mass loss). The boron containing samples evolved less CO and at a slower rate than the soybean oil copolymer, according to a condensed phase fire retardant mechanism. The silicon containing samples evolved more CO at a faster rate than the heteroatom free copolymer. This could indicate that the presence of silicon as a reactive or additive fire retardant has a more important effect in the vapour phase.[24]
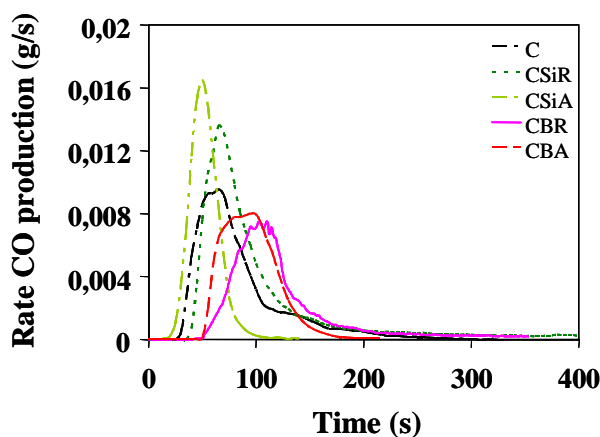
Figure 5. CO evolution vs. time for copolymers.

Dynamic mechanical thermal analysis (DMTA)

The DMTA data (Figure 6) obtained showed that chemical bonding of the silicon and boron moiety to the polymer backbone had a small effect on the T_g value. The copolymers appear to be composed of hard aromatic rich phases and soft oil rich phases with a certain amount of oligomers and unreacted monomers that act as plasticisers, thus causing a shift of the T_g to lower temperatures. On the other hand, the physical incorporation of silicon and boron additives into the polymer system resulted in a significant reduction in the mechanical properties of the system. As can be seen, the incorporation of high amounts of additives into the polymer has an important plasticising effect that causes a broadening of the Tan δ.
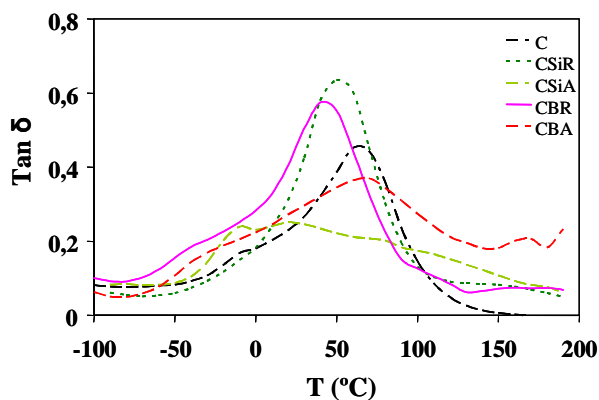
Figure 6. Tan δ of the copolymers as a function of temperature.

CONCLUSIONS

The development of new materials from renewable sources is essential if current levels of consumption are to be supported in a sustainable manner. In order to avoid compromising fire safety, it is necessary to develop fire retardant strategies for these new materials. Since most fire retardant formulations are polymer specific, it is necessary to investigate both the burning and decomposition behaviour of such new systems, in order to develop materials meeting current specifications. The incorporation of reactive fire retardant monomers containing boron and silicon has shown potential in these novel polymer systems.

Limiting oxygen index tests give useful information about the ignitability of the material, while cone calorimetry gives information on both the ignitability, and the burning behaviour. The cone calorimetry experiments gave much clearer evidence than the LOI measurements that incorporation of Si or B into the soybean oil copolymer resulted in fire retardation. This indicates the formation of a protective layer following ignition, reducing the rate of gas-phase fuel formation. The boron-containing copolymers were found to be the more efficient flame retardants for this system than were the silicon-containing copolymers. Moreover, the reactive or additive approach is a significant factor in terms of the level of fire retardance achieved.

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2.4. Rapid Soybean Oil Copolymers Synthesis by Microwave-Assisted Cationic Polymerization

Rapid Soybean Oil Copolymers Synthesis by Microwave-Assisted Cationic Polymerization

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ABSTRACT

Soybean oil is one of the most promising renewable raw materials for polymers. Cationic copolymerization with a variety of olefinic monomers gives interesting materials but the curing process is tedious and high temperatures and long reaction times are needed. We studied the cationic homopolymerization of soybean oil and its copolymerization with styrene and divinylbenzene under microwave irradiation using boron trifluoride diethyl etherate as initiator and the comparison with conventional heating showed a great enhancement in reaction rates.

Keywords: microwave curing, cationic copolymerization, biopolymers, vegetable oils, renewable resources.

INTRODUCTION

There is an urgent need to develop new synthetic routes to polymeric materials using renewable resources. Shifting society's dependence away from petroleum to renewable biomass resources is generally viewed as an important contribution to the development of a sustainable industrial society and effective management of greenhouse gas emissions. Petrochemical feedstocks will be depleted within next hundred of years and oil prices are ever increasing and subject to socio-political influences. Polymers from renewable resources will play an increasing role not only because of economical and environmental benefits, but also from the new property profiles that renewable resource polymers can exhibit, such as biocompatibility and biodegradability.[1]

The development of polymers from natural products is driven on several fronts. One of the more stimulating facet of this field is the search for new applications of vegetable oils, based on enhancing their specific reactivity in a given type of polymerization process.[2] Vegetable oils are triglycerides of different fatty acids with varying degrees of unsaturation, being the C=C double bonds susceptible to cationic polymerization. Among the Lewis acids capable of initiating the polymerization, BF_3OEt_2 has proved to be the most efficient initiator.[3] However, cationic homopolymerization of regular vegetable oils or the corresponding conjugated oils affords only low molecular weight viscous oils or soft rubbery materials of limited utility and olefinic monomers as styrene, divinylbenzene, norbornadiene or dicyclopentadiene are usually copolymerized with vegetable oils to overcome

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these drawbacks.[4] Other monomers such as a silicon-containing styrene derivative was copolymerized to obtain soybean-oil based copolymers with improved flame retardant properties.[5] Due to the poor miscibility between the soybean oils and the initiator and the large difference in the reactivity of the soybean oils and the comonomer, heterogeneous reactions occur at the early stages of the copolymerization, leading to a phase separated materials. Homogeneous copolymerization of soybean oils with styrene and divinylbenzene can be achieved using $BF_3.OEt_2$ modified with methyl oleate[5] or Norway fish oil ethyl ester[6] as initiator, as both are miscible with vegetable oils and styrenic monomers. The gel time of these systems varies from few minutes to several hours, depending on the stoichiometry and curing temperature.[7] Approximately 20-50 w% of the soybean oil reactants are converted into crosslinked polymers at gelation and fully cured thermosets are obtained after curing at elevated temperatures. The reaction mixture is heated for a given time at the appropriate temperatures, usually 12h at room temperature, followed by 12h at 60ºC and then 24h at 110ºC. In these systems, the maximum amount of triglyceride is incorporated into the crosslinked polymers when the soybean oil constitutes about 45-50 w% of the reactants.[6, 7]

Microwave irradiation has been shown to be a promising alternative heat source for organic transformations and polymerization reactions.[8] Microwave technology mainly owes its popularity to the enhanced reaction rates, higher yields and greater purity of the products. The enhanced reaction rates can be explained by the high reaction temperature that stems from a list of advantages over conventional heating, such as noncontact heating,

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circumventing the decomposition of molecules close to the walls of reaction vessel, instantaneous and rapid heating, resulting in a uniform heating of the reaction mixture, and highly specific heating, with the material selectivity emerging from the wavelength of microwave irradiation that intrinsically excites dipolar oscillation and induces ionic conduction. Moreover, the better progress of the chemical reactions is often a consequence of the high pressure achieved in sealed vessels. Besides the advantages of fast and homogeneous heating as well as the possible high temperature chemistry, non thermal microwave effects due to specific heating of polar intermediates have been observed, leading to modified selectivities and enabling reactions that cannot be performed under thermal heating.[9]

The use of microwave irradiation in polymer chemistry is an emerging field of research and a number of examples of step-growth, ring-opening and radical polymerizations can be found in the literature.[10-13] The objective of this work was to explore the cationic copolymerization of soybean oil, styrene and divinylbenzene under microwave assistance. First experiments were focused on the cationic polymerization of soybean oil with and without microwave irradiation to compare conversion in different conditions. In extension, we have examined the copolymerization of soybean oil, styrene and divinylbenzene to investigate how microwave irradiation influences reaction rate, monomer reactivity ratios and polymer properties.

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EXPERIMENTAL

Materials

The soybean oil employed in this study was supplied by Aldrich Chemical and has been used without further purification. It is primarily composed of unsaturated linoleic (C18:2), oleic (C18:1) and linolenic (C18:3) acids as well as saturated stearic (C18:0) and palmitic (C16:0) fatty acids. The content of other saturated and unsaturated fatty acids is negligible. ^{1}H NMR spectrum of soybean oil shows signals at 5.4-5.2 ppm (characteristic for olefinic hydrogens and for the methine protons of the glycerin backbone), at 4.2 and 4.1 ppm (corresponding to the diastereotopic protons of the glycerin methylene units), at 2.7 ppm, attributed to the methylene protons between two carbon-carbon double bonds), at 2.3 ppm (assigned to the methylene protons adjacent to the carbonyl groups), and at 2.1 ppm (characteristic of the methylene protons adjacent to the carbon carbon double bonds). Degree of unsaturation, expressed as the number of carbon-carbon double bonds per triglyceride, was 4.7 as obtained from the iodine index value and 4.5 as obtained from ^{1}H NMR spectroscopy (calculated from the area of the signal at 5.4-5.2 ppm and that of the peak at 4.2-4.1 ppm)

Styrene (ST) and divinylbenzene (DVB) were purchased from Fluka and washed with a NaOH 10% solution and then with water prior to use. The distilled-grade boron trifluoride diethyl etherate (BF$_3$OEt$_2$) used to initiate cationic polymerizations of the soybean oil was supplied by Aldrich. Methyl oleate (MeOL) was purchased from Alfa Aesar and was used to modify the original initiator, boron trifluoride diethyl etherate.

General procedure for cationic copolymerization with and without microwave irradiation

The desired amounts of styrene and divinylbenzene were added to the soybean oil. The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of a modified initiator. The modified initiator was prepared by mixing methyl oleate with the original initiator, boron trifluoride diethyl etherate (molar ratio BF_3OEt_2:MeOL 1.1:1.0). Samples were placed into a 5 mm (internal diameter) glass vials.

For conventional heating polymerizations, the reaction mixtures were heated for a given time at the appropriate temperatures. For microwave polymerizations, glass vials were placed inside the microwave reactor (10 mL) and subjected to microwave irradiation. Overheating of the reaction mixtures was avoided by cooling with compressed air. Curing conditions are listed in Figure 1 and Tables 1 and 2.

The soybean oil copolymers cured with and without microwave irradiation have been obtained in quantitative yields. To determine the soluble and insoluble fractions, a 0.5 g sample of the bulk polymer was extracted for 24 h with 200 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation and subsequent vacuum drying. The soluble substances and insoluble solids were dried under vacuum until constant weight and isolated for further characterization.

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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. The NMR spectra of the oil samples were recorded on a Varian Gemini 400-MHz spectrometer at room temperature using TMS as the internal standard. Molecular weights were determined using a Waters size exclusion chromatography (GPC) device equipped with a Waters 510 pump and a Shimadzu RID-6A refractive-index detector. The system was operated with three columns (K80M, Plgel mixed-D and Plgel mixed-E) at a nominal flow rate of THF 1.0 mL/min with a sample concentration of 0.5% in THF as solvent and toluene as internal standard. Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 5 mm diameter and 10 mm long were tested in a three point bending configuration. The thermal transitions were studied between -100 and 200ºC at a heating rate of 3ºC/min and a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

As mentioned above, the cationic polymerization of soybean oil using BF_3 as initiator under conventional heating conditions produces viscous oils. Their reactivity toward cationic homopolymerization is rather low and the initiator has been found immiscible with the oil, thus the conversion to high molecular weight polymers has proven relatively difficult. Completely

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homogeneous media can be obtained when the initiator is modified by mixing with methyl oleate (molar ratio BF_3OEt_2/MeOL 1.1:1.0). Cationic polymerization of soybean oil was performed using different amounts of BF_3OEt_2/MeOL as initiator (1, 2, 3 and 6 mol % based on C=C double bonds) under conventional heating at 70 and 140ºC. Samples which appear as soluble low molecular weight viscous oils were obtained at different reaction times. The degree of unsaturation, as obtained by ^{1}H NMR spectroscopy, decreases when increasing initiator concentration, being this decrease more pronounced at high reaction temperature (Figure 1a). The minimum values are obtained at 140ºC using 6 w% of initiator and for reaction times longer than 24h.

Cationic polymerization of soybean oil was also performed under microwave irradiation using different amounts of BF_3OEt_2/MeOL as initiator (1, 2, 3 and 6 mol % based on C=C double bonds). Different constant power inputs were applied and an IR prove was used to monitor the temperature of the microwave vial. In this way, by fixing a maximum temperature and pressure the system is switched off when the chosen parameters are exceeded.

To compare the microwave-induced crosslinking with that produced by thermal treatment, polymerizations were carried out under different experimental conditions in order to maintain a near constant temperature throughout the course of the reaction. Initially, the samples were irradiated with 150W for 120 min reaching a temperature of 70ºC and as a result, the starting soybean oil was recovered. To enhance the conversion of the oil to a

crosslinked material, all samples were irradiated at 300 W for 60, 120, 210 and 270 min reaching a temperature of 110ºC. In all cases, low molecular viscous oils were obtained and further analyzed by ^{1}H NMR spectroscopy.
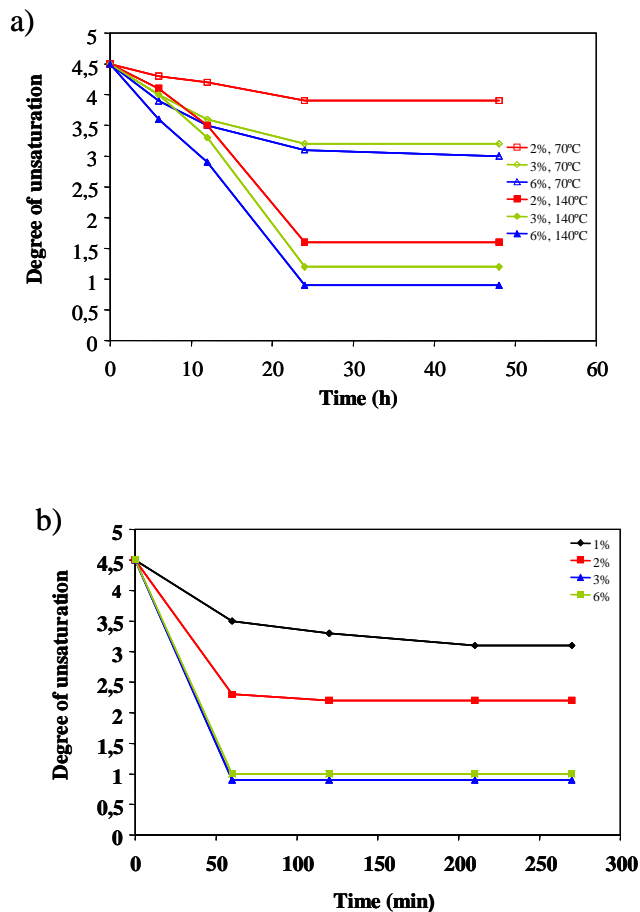
Figure 1. Variation of the degree of unsaturation in the polymerization of soybean oil initiated by different amounts of $BF_3.OEt_2/MeOL$, (a) conventional heating (70 and 140ºC), (b) microwave curing (300 W).

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As expected, the degree of unsaturation decreases as the amount of initiator increases. A similar effect can be observed when the time of irradiation increases (Figure 1b). The minimum values of unsaturation degrees obtained are similar to the ones obtained by conventional thermal curing, but the reaction times needed to achieve these conversions are much lower. The molecular weight of the oligomeric materials was determined by GPC. Figure 2a shows a series of chromatograms of polymers obtained by curing at 300 W for 210 min with different initiator amounts. The results indicate that several components of different molecular weights exist. When using 1w% of initiator, an intense peak (peak 2) can be observed, with a molecular weight corresponding to starting soybean oil by comparative GPC analysis of pure starting material. Its intensity decreases and a shoulder at higher molecular weights appears (peak 1) as the amount of initiator increases, thus indicating that the cationic polymerization through the triglyceride double bonds is taking place. From GPC data, no increase in the molecular weight is achieved when increasing the amount on initiator from 3 to 6 mol%. Peak 3, corresponding to lower molecular weights, can be attributed to methyl oleate and fatty acid components from the acid catalyzed hydrolysis during the polymerization. Its intensity seems to be constant, indicating that these compounds are not incorporated into the polymer even when the amount of initiator increases. Figure 2b shows a series of chromatograms of polymers obtained using 3 w% of initiator by curing at 300 W for different reaction times. No increase in molecular weight is observed for reaction times longer than 60 min, according to the decrease of the unsaturation degree showed in Figure 1.

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By comparing experiments with and without microwave irradiation, no increase in soybean oil conversion is observed under microwave irradiation compared to the conventional heating reactions. However, the acceleration of the reaction is noteworthy and polymerization proceeds 24 times faster than in conventional heating conditions.
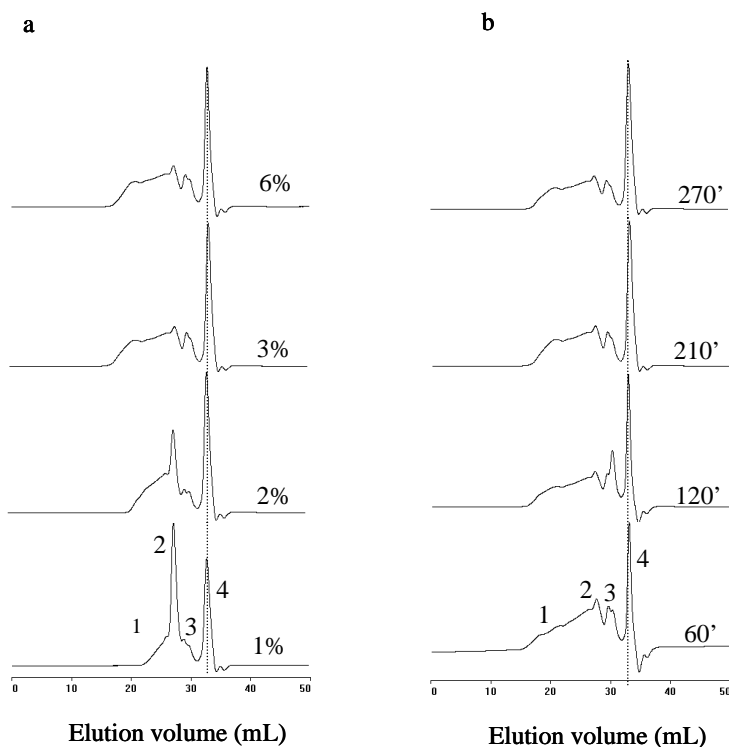
Figure 2. GPC chromatograms of soluble fraction after microwave induced polymerization of soybean oil initiated by BF_3OEt_2/MeOL, (a) with different initiator concentration (300 W, 210 min), (b) at different reaction times (300 W, 3%w BF_3OEt_2).

In view of the faster monomer conversion, we examined the effect of microwave irradiation on the crosslinking of soybean oil, styrene and divinylbenzene. Curing reactions have been described to proceed slightly faster under microwave irradiation during the early stage of the process.[14] 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, in 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.[15, 16] In this case, styrene and divinylbenzene are non polar whereas soybean oil has a higher polarity. These differences of monomer polarities could yield modification of copolymerization behaviour by microwave irradiation.[17]

The initiator was obtained as previously mentioned by mixing BF_3OEt_2 with MeOL and homogeneous reactions were generated from a mixture of soybean oil, styrene and divinylbenzene in a molar ratio 1.00:6.00:2.25. This composition was chosen because it approximates the composition of maximum oil incorporation as described in the literature for this system.[6] The amount of BF_3OEt_2 was kept constant at 3 mol% based on the total C=C double bonds in the polymerization mixture (molar ratio BF_3OEt_2/MeOL 1.1:1.0). To compare, a set of copolymerizations were carried out under

conventional heating conditions (Table 1). As can be seen, post curing at 110ºC for 12h is needed to reach materials with a high content of insoluble fractions. To further characterize the crosslinking reaction, we analyzed the soluble fractions by ^{1}H NMR spectroscopy. From the peak areas of the aromatic protons signal (broad signal centered at 7.0 ppm) and the glycerine methylene protons (4.2 ppm) it is possible to calculate the molar ratio of the aromatic and oil components. As can be seen, the aromatic content of the soluble fraction is in all cases much lower that the expected from the initial copolymerization mixture, and, consequently, there is a higher content of aromatic materials in the insoluble fraction. This is attributed to the fact that styrene and divinylbenzene have higher reactivity than soybean oil. There are not significant differences in the amount of the aromatic part of the soluble fraction when increasing reaction time or performing a postcuring.

Table 1. SOY/ST/DVB copolymers obtained by conventional heating.

Sample	Curing conditions	Soluble fraction [a] w %	Insoluble fraction [a] w %	Aromatic material [b] w %	
				Soluble fraction	Insoluble fraction
1	2h, 60ºC	39.1	60.9	6	73
2	6h, 60ºC	37.6	62.4	7	71
3	12h, 60ºC	32.5	67.5	8	66
4	6h, 60ºC + 12h, 110ºC	22.8	77.2	6	59
5	12h, 60ºC + 12h, 110ºC	19.4	80.6	7	56

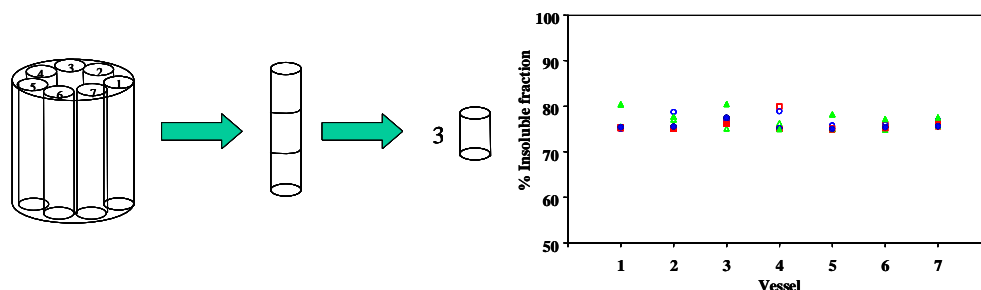[a] Weight percentage of the soluble and insoluble fractions after Soxhlet extraction with methylene chloride.

[b] The weight percentage of aromatic materials in the feed was 47. The weight percentage of aromatic materials in the extracted soluble fraction is calculated from the 1H NMR spectra. Data for the insoluble fraction have been calculated indirectly from these values.

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Monomodal microwave ovens have wave guides which focus the microwaves in a linear and uniform fashion onto the sample, but differences in the size and shape of the samples is a factor that may affect the properties of the microwave cured samples: the temperature at the center of the sample is higher than that of the sample boundaries because of the slow heat conduction inside the sample. To verify the reproducibility of the microwave induced polymerization we carried out a systematic study of the crosslinking reaction by introducing seven glass vials containing 1.5 g of the polymerization mixture into the microwave oven cavity. To further study the reproducibility of the process, after curing each sample was divided in three fractions and the amount of polymer that remained insoluble after extraction with methylene chloride as refluxing solvent was quantified (see Figure 3).

A similar experience was carried out with 3.0 g samples. Polymerizations were carried out by irradiation at 150 W for 30 min followed by irradiation at 300 W for 30 min. The cured soybean oil copolymers have been obtained in essentially quantitative yields. All the copolymers appear as clear to dark-yellow rubbery materials at room temperature, with range from tough and ductile to very soft rubbers. As can be seen in Figure 3, yield of insoluble material ranges from 75-80% and no significant differences among samples from the seven vials, in both experiences, and the six fractions can be observed.

These results imply that the size and the shape of the sample seem not to affect the crosslinking degree of the copolymers in the explored reaction conditions.

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Figure 3. Yield of insoluble polymer after microwave induced copolymerization of soybean oil, styrene, divinylbenzene initiated by BF_3OEt_2. Seven glass vials containing different amounts (either 1.5 or 3.0 g) of the polymerization mixture were introduced into the microwave oven cavity and after curing each sample was divided in three fractions (six measurements for each vessel). Curing was carried out at 150 W for 50 min followed by irradiation at 300 W for 30 min).

To select the microwave curing conditions, we carried out the copolymerizations collected in table 2. In all cases, reached temperatures at curing and postcuring steps were 70 and 110ºC respectively. As can be seen, increasing irradiation power for a given reaction time does not increase the content of insoluble fraction. In a similar way, postcuring at higher irradiation powers does not affect significantly the yield of crosslinked material, that in all cases ranges about 80%. The aromatic content of the soluble fraction increases and consequently the aromatic content of the insoluble fraction decreases, thus indicating that the oil incorporation in the crosslinked network increases as the extension of curing increases. When comparing to samples obtained by conventional heating with similar soluble and insoluble content (samples 4 and 5), slight differences can be observed

on the aromatic content of the insoluble fractions. However, it is noteworthy
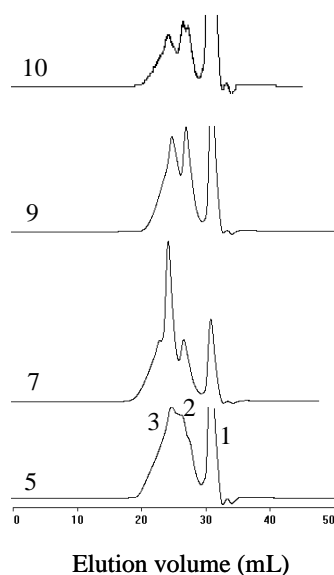that these materials are obtained eight-fold faster than conventionally heated
materials.

Table 2. SOY/ST/DVB copolymers obtained by microwave irradiation.

Sample	Curing conditions	Soluble fraction [a] w %	Insoluble fraction [a] w %	Aromatic material [b] w %	
				Soluble fraction	Insoluble fraction
6	150 W, 60 min	19.9	79.3	10	57
7	300 W, 60 min	18.4	80.1	10	56
8	150 W 60 min + 300 W 60 min	17.1	82.3	10	55
9	150 W 120 min + 300 W 60 min	14.4	83.8	15	53
10	150 w 60 min + 300 W 120 min	15.9	83.9	20	52

[a] Weight percentage of the soluble and insoluble fractions after Soxhlet extraction with methylene chloride.

[b] The weight percentage of aromatic materials in the feed was 47. The weight percentage of aromatic materials in the extracted soluble fraction is calculated from the ^{1}H NMR spectra. Data for the insoluble fraction have been calculated indirectly from these values.

The soluble fractions were analyzed by GPC (Figure 4, samples 7, 9 and
10). The intense peak 1 corresponding to soybean oil decreases and a
shoulder at higher molecular weights appears as the reaction time increases,
thus indicating that oligomerization is taking place. No significant differences
on molecular weight of the soluble fractions can be observed when
comparing to samples obtained by conventional heating (sample 5).

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Figure 4. GPC chromatograms of soluble fractions from the copolymerization of soybean oil, styrene and divinylbenzene initiated by BF_3OEt_2/MeOL (samples 5, 7, 9 and 10, table 2).

DMA has been used to investigate the dynamic mechanical behavior of the copolymers. Figure 5 shows the storage moduli and the tan δ values of samples cured under conventional heating (samples 4 and 5) and under microwave irradiation (samples 9 and 10). At temperatures below -50ºC the copolymers are in the glassy state and their storage moduli decrease slightly with increasing temperature. A rapid decrease in the E' value of roughly 4 orders of magnitude is observed in the temperature range from –20 to 80 ºC, corresponding to the primary relaxation process of the copolymers. The energy dissipation associated to the modulus decrease can be seen as a maximum in the tan δ versus T curve. The modulus reaches a plateau at higher temperatures which is assigned to the rubbery state. No significant

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differences can be observed among the different samples. The presence of the rubbery plateau in the DMA curve is evidence for the existence of a stable crosslinked network and according to the kinetic theory of rubber elasticity, the crosslinking density of the copolymer can be determined from the rubbery moduli using the following equation E'= 3νRT where E' is the storage modulus of the crosslinked copolymer in the rubbery region above the glass transition temperature, R is the universal gas constant and T is the absolute temperature.
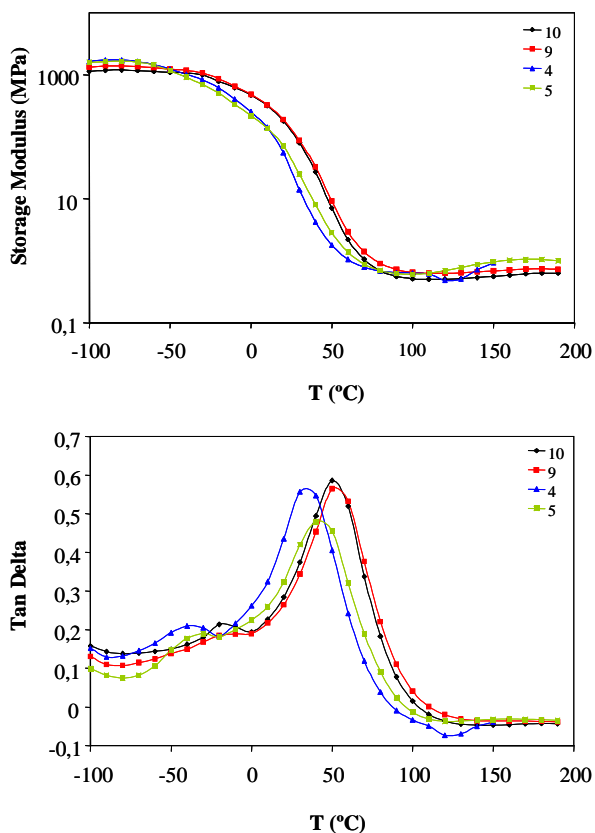
Figure 5. Storage modulus (E') and loss factor (tanδ) of copolymers obtained by microwave curing and conventional curing (samples 4, 5, 9 and 10, tables 1 and 2).

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Rubber elasticity theory is not expected to completely apply to the highly crosslinked polymers, but should show general trends in how crosslinking density is affected by the curing process. The values of the storage moduli E' used for calculations were taken at 50ºC above the Tg. The crosslinking density of the samples ranges from 67.5 to 74.3 mol/m^3 and there are not significant differences among the samples, in agreement with the insoluble content reported in tables 1 and 2. Since the storage modulus is a manifestation of the crosslinking density and hence of the network stiffness, this must be also due to the similar aromatic content in the insoluble fraction and to the similar incorporation of the triglyceride chains into the network. From the tan δ plots of figure 5, the presence of a shoulder indicates that the systems have two glass transition temperatures which merge into a very broad transition. The copolymers appear to be complex heterogeneous systems composed of hard aromatic rich phases and soft oil rich phases, with certain amount of unreacted monomers which act as plasticizers. The high temperature transition (from 53 to 34ºC) corresponds to the glass transition temperature of the plasticized aromatic rich phase, while the low temperature transition is attributed to the plasticized oil rich phase. There is a slight shift of both the higher and the lower transition temperatures to lower values for the samples cured by conventional heating. This could be due to the slightly higher soluble fraction for the first transition and the significantly lower aromatic content of the soluble fraction for the second one, in the case of samples 4 and 5. The heights of the tan δ peaks are not significantly different, indicating similar crosslinking densities and segmental mobilities. In the same way, broadening of the tan δ peaks caused by the plasticizing effect of the oil rich phase is similar.

CONCLUSIONS

In conclusion, the copolymers obtained under conventional heating and under microwave irradiation show similar content and compositions of soluble and insoluble fractions. DMA analysis indicates that the dynamic mechanical behavior of the materials is very similar. However, we have observed a noticeable acceleration of cationic polymerization of soybean oil and cationic copolymerization of soybean oil, styrene and divinylbenzene when performed under microwave irradiation. So, the curing time was considerably shortened under microwave irradiation what makes this approach very useful to develop new polymers from vegetable oils as renewable resources.

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2.5. Approaches to Phosphorus-Containing Soybean Oil Copolymers. Cross-Metathesis of Fatty Acid Derivatives as an Alternative Way to Phosphorus-Containing Reactive Flame Retardants

Approaches to Phosphorus-Containing Soybean Oil Copolymers. Cross-Metathesis of Fatty Acid Derivatives as an Alternative Way to Phosphorus-Containing Reactive Flame Retardants

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ABSTRACT

Two different approaches to phosphorus containing soybean oil copolymers were investigated. First, two phosphorus containing styrene derivatives (dimethyl-*p*-vinylbenzylphosphonate (DMVBP) and diphenyl styryl phosphine oxide (DPSPO)) where used as comonomers in the cationic copolymerization of soybean oil, styrene and divinylbenzene, obtaining heterogeneous systems in all cases. To overcome this drawback, the cross-metathesis reaction of methyl 10-undecenoate and DMVBP was carried out to link the phosphorus moiety to the vegetable oil derivative. This second approach permitted the synthesis of a new reactive phosphorus-containing plant oil derivative, which was incorporated to the soybean oil, styrene and divinylbenzene system. The cationic copolymerization was investigated and the structure, thermal stability and mechanical and flame retardant properties of the resulting copolymers were studied. Thermosets with glass transition

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temperatures of 66 and 59ºC and with LOI values of 23.1 and 24.0 were obtained, showing that the fire retardant properties of soybean oil based copolymers are improved by adding covalently bonded phosphorus to the thermosets.

Keywords: vegetable oils, renewable resources, cationic copolymerization, phosphorus-containing polymers, metathesis

INTRODUCTION

One of the biggest challenges in polymer science is to find replacements for the rapidly decreasing fossil feedstocks. The utilization of renewable resources as raw materials for the production of monomers and polymers can contribute to the sustainable development, not only because it decreases CO_2 emissions and avoids contributions to green house effects but also because it can meet other advantages as biodegradability and low toxicity. Polymers from renewable resources will play an increasing role because of economical and environmental benefits and the new property profiles that renewable resource polymers can exhibit, such as biocompatibility and biodegradability.[1]

Vegetable oils are one of the cheapest and most abundant annually renewable natural resources. They are available in large quantities from various oilseeds and are now being used in an increasing number of industrial applications. Recently, there have been many attempts to convert vegetable

oils and fatty acids to useful polymers.[2] One of the more stimulating facet of this field is the search for new applications of vegetable oils, based on enhancing their specific reactivity in a given type of polymerization process. Vegetable oils are triglycerides of different fatty acids with varying degrees of unsaturation, being the C-C double bonds capable of undergo cationic polymerimerization. Among the Lewis acids capable of initiating the polymerization, BF_3OEt_2 has proved to be the most efficient initiator.[3] However, cationic homopolymerization of regular vegetable oils or the corresponding conjugated oils affords only low molecular weight viscous oils or soft rubbery materials of limited utility. Thus, olefinic monomers as styrene, divinylbenzene, norbornadiene or dicyclopentadiene are usually copolymerized with vegetable oils to overcome these drawbacks.[4] Moreover, like other organic polymers, a factor limiting the use of oil-based polymers is their flammability. The synthesis and characterization of flame-retardant polymers from bromoacrylated plant oil triglycerides has been reported,[5] but resins that contain bromine release hydrogen bromine during combustion, which causes corrosion and toxicity. For this reasons, the search is now on new environmentally friendly flame-retardant polymeric materials. Phosphorus- and silicon-containing polymers are well recognized for their flame retardant properties[6] and they are increasingly becoming more popular than their halogen counterparts as they generally give off nontoxic combustion products. In a previous paper, we described the incorporation of an organosilicon functionality to soybean oil based polymers.[7] Their properties suggest that the resulting materials may prove to be useful alternatives for current non renewable-based thermosets and that the flame-

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retardant properties of vegetable oil based thermosets can be improved by adding covalently bonded silicon to the polymer.

The aim of this work was to extend the application possibilities of vegetable oil-based thermosets by improving their flame retardance and to preserve the environmentally friendly character of these materials by using a phosphorus based system instead of a halogen based system. We investigated the influence of two phosphorus containing styrene derivatives (dimethyl-p-vinylbenzylphosphonate (DMVBP) and diphenyl styril phosphine oxide (DPSPO) in the cationic copolymerization of soybean oil, styrene and divinylbenzene, obtaining heterogeneous systems in all cases. We then carried out the cross-metathesis reaction of methyl 10-undecenoate and DMVBP to attach the phosphorus moiety to the vegetable oil derivative and incorporated this reactive phosphorus derivative to the soybean oil, styrene and divinylbenzene system. The cationic copolymerization of this curing system has been investigated and the structure, thermal stability and mechanical and flame retardant properties of the resulting copolymers have been studied.

EXPERIMENTAL SECTION

Materials

The soybean oil employed in this study was supplied by Aldrich Chemical and has been used without further purification. It is primarily composed of unsaturated linoleic (C18:2), oleic (C18:1) and linolenic (C18:3) acids as well as saturated stearic (C18:0) and palmitic (C16:0) fatty acids. The content

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of other saturated and unsaturated fatty acids is negligible. ^{1}H NMR spectrum of soybean oil shows signals at 5.4-5.2 ppm (characteristic for olefinic hydrogens and for the methyne protons of the glycerin backbone), at 4.2 and 4.1 ppm (corresponding to the diastereotopic protons of the glycerin methylene units), at 2.7 ppm, attributed to the methylene protons between two carbon-carbon double bonds), at 2.3 ppm (assigned to the methylene protons adjacent to the carbonyl groups), and at 2.1 ppm (characteristic of the methylene protons adjacent to the carbon carbon double bonds). Degree of unsaturation, expressed as the number of carbon-carbon double bonds per triglyceride, was 4.7 as obtained from the iodine index value and 4.5 as obtained from ^{1}H NMR spectroscopy (calculated from the area of the signal at 5.4-5.2 ppm and the area of the signal at 4.2-4.1 ppm)

Styrene (ST) and divinylbenzene (DVB) were purchased from Fluka and washed with a NaOH 10% solution and then with water prior to use. The distilled-grade boron trifluoride diethyl etherate (BF_3OEt_2) used to initiate cationic polymerizations of the soybean oil was supplied by Aldrich. Methyl oleate (MeOL) was purchased from Alfa Aesar and was used to modify the original initiator, boron trifluoride diethyl etherate. 4-bromostyrene, 4-vinylbenzylchloride, 10-undecenoic acid, butyllitium (2.5M in hexane), chlorodiphenylphosphine, sodium hydride (60% in mineral oil), dimethyl phosphite, benzylidene–*bis*(tricyclohexylphosphine) dichlororuthenium (C1, Grubbs catalyst 1st generation), benzylidene [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium (C2, Grubbs catalyst 2nd generation) were purchased from Aldrich. The solvents were purified using standard procedures.

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Synthesis of diphenyl styryl phosphine oxide (DPSPO)[8]

A dry two-necked 250 mL round-bottomed flask, equipped with a magnetic stirrer, was purged with N_2 and anhydrous tetrahydrofuran (65 mL) was added. The flask was cooled to -78ºC and BuLi (54.6 mmol) was added. 4-bromostyrene (54.6 mmol) was added dropwise and the reaction was stirred for 2 h at -78ºC. After that, chlorodiphenylphosphine (54.6 mmoL) was added dropwise at -78ºC and the reaction was allowed to reach room temperature and was stirred overnight. At the end of the reaction the mixture was washed twice with a saturated solution of NH_4Cl and twice with brine. The aqueous layer was extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Diphenyl styryl phosphine was dissolved in dichloroethane (40 mL) and oxidized with a saturated aqueous solution of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) maintaining the temperature below 30ºC. The reaction was followed by TLC (methanol/ethyl acetate, 2:3) until disappearance of starting material (1h). A solution of $Na_2S_2O_5$ was added until the oxidant reagent was consumed. A large excess of water was added and layers separated. The product was extracted with dichloromethane and the organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure obtaining a solid that was dissolved in dichloromethane and precipitated in hexane. The product was obtained in a 65% yield.

^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 5.38 (dd, J_{cis}=11.2 Hz, J_{gem}=0.8 Hz, CH=CH_2), 5.86 (dd, J_{trans}=17.6 Hz, J_{gem}=0.8 Hz, CH=CH_2), 6.74 (dd, J_{trans}=17.6 Hz, J_{cis}=10.8 Hz, CH=CH$_2$), 7.44-7.69 (m, H$_{ar}$).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 116.73 (s, CH=CH2), 126.31 (d, C$_{ar,orto}$, J=12.2 Hz), 128.62 (d, C$_{ar,metaP}$, J=12.3 Hz), 132.10-132.40 (C$_{ar,meta}$, C$_{ipso}$, C$_{ar,ortoP}$), 132.51 (s, C$_{ipsoP}$), 132.98 (C$_{ipsoP}$), 135.94 (CH=CH$_2$), 141.12 (C$_{ipso}$).

^{31}P (CDCl$_3$, TMS, δ in ppm): 29.76.

Synthesis of dimethyl-p-vinylbenzylphosphonate (DMVBP)[9]

A two-necked round-bottom flask equipped with a condenser and a magnetic stirrer was charged, under inert atmosphere with 170 mL of anhydrous tetrahydrofuran and 5.04 g (0.246 mol) of sodium hydride. The whitish suspension was cooled to 0ºC under magnetic stirring. To this solution, 19.0 g of dimethyl hydrogen phosphonate (0.172 mol) was added slowly. Hydrogen evolution was observed. At the end of the addition, the mixture was taken to room temperature. A solution of 28.50 g of vinylbenzyl chloride (0.259 mol) in anhydrous THF and 2.46 g of sodium iodide (16.4 mmol) were added dropwise to the mixture at 0ºC. After addition the mixture was allowed to reach to room temperature and was stirred overnight. The salt formed was removed by precipitation from ethyl acetate and filtration. The filtrate was concentrated and the product obtained was purified by silica gel column chromatography using hexane-ethyl acetate 1:2 and then ethyl acetate as eluent. The yield was 80%.

^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 3.16 (d, J=21.6 Hz, CH$_2$-P), 3.67 (d, J=10.4 Hz, OCH$_3$), 5.24 (dd, J_{cis}=10Hz, J_{gem}=0.8 Hz, CH=CH_2), 5.73 (dd,

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J_{trans}=17.2 Hz, J_{gem}=0.8 Hz, CH=CH_2), 6.69 (dd, J_{trans}=17.6 Hz, J_{cis}=11.2 Hz, CH=CH$_2$), 7.25 (d, J=8 Hz, H$_{ar,meta}$), 7.36 (d, J=7.6 Hz, H$_{ar,orto}$).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 32.72 (d, J=138.0 Hz, CH$_2$-P), 53.05 (d, J=6.9 Hz, OCH$_3$), 113.97 (s, CH=CH$_2$), 126.60 (d, J=3.0 Hz, C$_{ar,orto}$), 129.97 (d, J=6.9 Hz, C$_{ar,meta}$), 130.77 (s, C$_{ipso}$), 130.87 (s, C$_{ipso}$), 136.45 (s, CH=CH$_2$).

^{31}P (CDCl$_3$, TMS, δ in ppm): 29.30.

Synthesis of dimethylbenzylphosphonate (DMBP)[9]

A two-necked round-bottom flask equipped with a condenser and a magnetic stirrer was charged, under an inert atmosphere, with 80 mL of anhydrous tetrahydrofuran and 2.1g (0.088 mol) of sodium hydride. The whitish suspension was cooled to 0ºC under magnetic stirring. To this solution, 10.5 g of dimethyl hydrogen phosphonate (0.095 mol) was added slowly. Hydrogen evolution was observed. At the end of the addition, the mixture was returned to room temperature. A solution of 15.0 g of benzyl chloride (0.088 mol) in anhydrous THF and 2.46 g of sodium iodide (16.4 mmol) was added dropwise to the mixture at 0ºC. After addition, the mixture was allowed to reach room temperature and was stirred overnight. The salt formed was removed by precipitation from ethyl acetate and filtration. The filtrate was concentrated and the product obtained was purified by silica gel column chromatography using hexane-ethyl acetate 1:2 and then ethyl acetate as eluent. The yield was 80%.

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^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 3.14 (d, J=21.6 Hz, CH$_2$-P), 3.63 (d, J=10.8 Hz, OCH$_3$), 7.21-7.33 (m, 5H).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 32.89 (d, J=138.8 Hz, CH$_2$-P), 52.95 (d, J=6.8 Hz, OCH$_3$), 127.07 (d, J=3.8 Hz, C$_{ar,para}$), 129.71 (d, J=3.8 Hz, C$_{ar,meta}$), 129.77 (d, J=6.8 Hz, C$_{ar,orto}$), 131.26 (d, J=9.1 Hz, C$_{ipso}$).

[31]P (CDCl$_3$, TMS, δ in ppm): 29.49.

Synthesis of Methyl 10-Undecenoate (MU)

To a 500 mL, round bottom flask, 60 g (0.3 mol) of 10-undecenoic acid, 300mL of methanol, and a few drops of concentrated sulfuric acid were added, and then the mixture was mechanically stirred and refluxed. The reaction was followed by thin-layer chromatography with the cloroform/methanol (9:1) system as eluent and the fluorescein/ Br$_2$ system as the dying agent. Once the reaction was completed, the crude was left to cool, and the methanol evaporated. The oily ester was distilled in vacuo (bp=54.6 - 55.0ºC at 0.1mmHg) and afforded a 91% yield.

^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 1.3 (m, 10H), 1.6 (m, 2H), 2.0 (m, 2H, CH$_2$-CH=), 2.3 (t, J = 7.7 Hz, CH$_2$CO), 3.6 (s, CH$_3$O), 5.0 (d, 1H, J_{cis} = 10.2 Hz, CH=CH$_2$), 5.04 (d, J_{trans} = 17.2 Hz, CH=CH2), 5.8 (m, CH=CH$_2$).

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^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 24.91 (CH$_2$-CH$_2$-CO), 28.84, 29.05, 29.11, 29.22, 29.33 (-CH$_2$-), 33.78 (CH$_2$-CO), 34.02 (CH$_2$-CH=), 51.43 (OCH$_3$), 114.14 (CH$_2$=CH), 139.17 (CH=CH$_2$), 174.39 (C=O).

Cross-Metathesis reactions

A mixture of methyl 10-undecenoate (MU) and 4-dimethylvinylbenzylfosfonate (DMVBP) in anhydrous CH$_2$CL$_2$ was placed in a two necked round bottom flask equipped with a reflux condenser. The required amount of the metathesis catalyst was then added. The resulting mixture was stirred at 45 ºC for 12 h under nitrogen atmosphere. The solvent was removed under reduced pressure and the MU and DMVBP were removed by distillation under vacuum (0.1 mm Hg). Then, the products of self-metathesis were separated by gradually eluting through a short pad of silica with hexane followed by ethyl acetate as eluents. The solvent was removed under reduced pressure.

MU-DMVBP: ^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 1.18-1.31 (m, 4H), 1.34-1.42 (m, 2H), 1.50-1.61 (m, 2H), 2.07-2.17 (m, 2H), 2.18-2.26 (t, 2H), 6.10-6.19 (m, 1H), 6.32 (d, 1H), 7.11-7.18 (m, 2H), 7.18-7.26 (m, 2H).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 25.14, (s, CH$_2$CH$_2$COOCH$_3$), 27.05 (s, CH$_2$CH=CH$_{cis}$), 29.34-29.50 (5C, CH$_2$), 32.78 (d, J=137.8 Hz, CH$_2$-P), 33.23 (s, CH$_2$CH=CH$_{trans}$), 34.30 (s, CH$_2$COOCH$_3$), 51.68 (s, OCH$_3$), 53.15 (d, J=6.8 Hz, POCH$_3$), 126.37 (d, J=3.12 Hz, C$_{meta}$-P), 129.42 (d, J=2.31 Hz, =CH-Ph), 129.67 (d, J=9.96 Hz, $C$$_{ipso}$-CH$_2$) 130.01 (d, J=6.84 Hz, C$_{orto}$-P), 131.50 (s, CH=CH-Ph), 136.25 (s, $C$$_{ipso}$-CH), 174.50 (s, C=O).

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^{31}P (CDCl$_3$, TMS, δ in ppm): 29.41 ppm.

DMVBP-DMVBP: ^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 3.2 (d, 4H, *J*=22 Hz), 3.7 (d, 12H, *J*=10.8 Hz), 7.1 (s, 2H), 7.3 (d, 4H, *J*=8.0 Hz), 7.5 (d, 4H, *J*=8.0 Hz).

^{13}C NMR (CDCl$_3$, TMS, δ in ppm): 32.89 (d, *J*=138.8 Hz, CH$_2$P), 53.16 (d, *J*=6.8 Hz, OCH$_3$), 126.96 (d, *J*=3.0 Hz, C$_{ipso}$-CH$_2$), 128.37 (s, CH=CH), 130.24 (d, *J*=6.8 Hz), 130.79 (d, *J*=9.9 Hz, Car), 136.25 (s, C$_{ipso}$-CH).

^{31}P (CDCl$_3$, TMS, δ in ppm): 29.24.

MU-MU: ^{1}H NMR (CDCl$_3$, TMS, δ in ppm): 1.20-1.37 (m, 20H), 1.55-1.69 (m, 4H), 1.90-2.05 (m, 4H), 2.30 (t, *J*=7.2 Hz), 3.66 (s, 6H), 5.32-5.42 (m, 2H).

^{13}C-NMR (CDCl$_3$, TMS, δ in ppm): 25.17 (CH$_2$), 27.05 (CH$_{2cis}$), 29.30 (CH$_2$), 29.36 (CH$_2$), 29.44 (CH$_2$), 29.51 (CH$_2$), 29.81 (CH$_2$), 32.79 (CH$_{2trans}$), 34.33 (CH$_2$), 51.68 (CH$_3$), 130.55 (CH=CH), 174.50 (C=O).

Cationic Copolymerization

The following reaction procedure was usually employed. The desired amounts of monomers were added to the soybean oil (Tables 1 and 2). The reaction mixture was vigorously stirred, followed by the addition of an appropriate amount of initiator (3 mol% of BF$_3$OEt$_2$ based on the total C=C double bond in the polymerization mixture). The initiator was prepared by mixing boron trifluoride diethyl etherate with methyl oleate (molar ratio

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BF$_3$OEt$_2$:MeOL 1.1:1.0). The reaction mixture was then injected into aluminium moulds and heated for a given time at the appropriate temperatures, usually 12 h at 80ºC and 12h 140ºC. To determine the soluble and insoluble fractions, a 0.5 g sample of the bulk polymer finely grounded was extracted for 24 h with 200 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation. The soluble substances and the insoluble solid were dried under vacuum until constant weight and isolated for further characterization.

Instrumentation

The NMR spectra of the samples were recorded on a Varian Gemini 400-MHz spectrometer (400 MHz for ^{1}H, 100.57 for ^{13}C and 161.9 MHz for ^{31}P). The samples were dissolved in deuterated chloroform, and spectra were obtained at room temperature using TMS as internal standard.

Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer with N$_2$ as the purge gas. The heating rate was 10ºC/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N$_2$ as the purge gas at scanning rates of 10°C/min. Mechanical properties were measured with a dynamic mechanical thermal analyzer (DMTA) (TA DMA 2928). Specimens 1.2 mm thick, 5 mm wide, and 10 mm long were tested in a three point bending configuration. The various thermal transitions were studied between -100 and 100ºC at a heating rate of 3ºC/min and a fixed frequency of 1 Hz.

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RESULTS AND DISCUSSION

The cationic polymerization of soybean oil using BF_3 as initiator produces viscous oils. Its reactivity toward cationic homopolymerization is rather low and the initiator has been found immiscible with the oil,[10] thus the conversion to high molecular weight polymers has proven relatively difficult. The copolymerization of soybean oil, styrene and divinylbenzene using boron trifluoride diethyl etherate is also heterogeneous, being the poor miscibility between the soybean oil and the initiator the main reason for the heterogeneity rather than the difference in the reactivity between the oil and the styrenic monomers. However, completely homogeneous reaction media can be obtained when the initiator is modified with fish oil ethyl esters.[3,11] In our case,[7] the initiator system was obtained by mixing methyl oleate with boron trifluoride diethyl etherate (molar ratio BF_3OEt_2/MeOL 1.1:1.0), and homogeneous reactions were generated from a mixture of soybean oil, styrene and divinylbenzene in a molar ratio 1.00:6.00:2.25. This composition has been chosen because it approximates the composition of the maximum oil incorporated into the polymer as described in the literature for this system.[11] The amount of BF_3OEt_2 was kept constant at 3 mol% based on the total C=C double bond in the polymerization mixture.

The copolymerization of styrene with a variety of comonomers containing covalently bound phosphorus, including vinylphosphonic acid, several dialkyl vinylphosphonates and various vinyl and allyl phosphine oxides has been described.[12] All these phosphorus-containing copolymers show flame retardant properties, but their behaviour indicates that the phosphorus environment plays an important role. Indeed, the P-C bond is more stable to

hydrolysis than the P-O-C bond and is broken just before the C-C bond because of its lower bond energy.[13] In our search for phosphorus containing comonomers with high thermal and chemical stability, we considered phosphine oxides. In this way, we used styrene and diphenyl styryl phosphine oxide (DPSPO) as major co-monomer and divinylbenzene as crosslinking agent for the cationic initiated polymerization of soybean oil (Scheme 1). DPSPO was obtained from 4-bromostyrene by reaction with BuLi and further addition of Ph$_2$PCl, followed by oxidation, according to the reported procedure.[14]
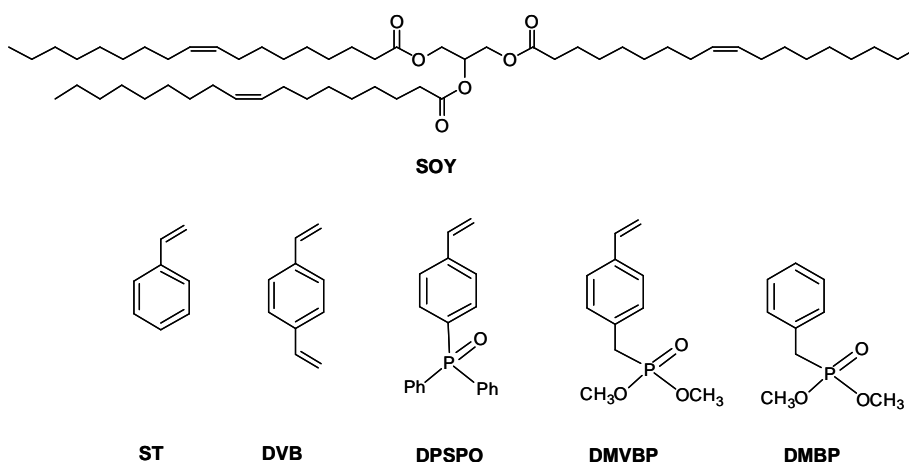
**Scheme 1.** Structures of the comonomers.

To obtain phosphorus-containing soybean oil based thermosets, a set of copolymerization mixtures were prepared. The DVB amount was kept constant as the ST + DPSPO amount, while the content of ST was decreased as the DPSPO was increased in order to obtain thermosets with different phosphorus contents.

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Samples were prepared by adding the desired amounts of ST, DPSPO and DVB to the soybean oil and the mixture was vigorously stirred. For all the compositions, the solid DPSPO remained insoluble even when heated to 50ºC. The reaction procedure was modified by mixing the phosphorus-containing monomer in the mixture of ST and DVB and further adding to the soybean oil. In another approach, soybean oil was mixed with DVB, and DPSPO with ST, and one mixture was slowly added to the other with stirring. These experiments lead to the formation of translucid mixtures with a suspension of fine particles in some cases. Even though the mixtures seemed not to be completely homogeneous, BF_3OEt_2/ MeOL was added as a cationic initiator to carry out the copolymerization. In all cases, a large number of small, solid particles appeared at the early stages of the reaction and precipitated. The obtained products were dark brown and heterogeneous.

Heterogeneous reactions are difficult to control experimentally. As a result, the densities are not identical in the final bulk polymers and the mechanical properties are different in various parts of the material. In our case, the phosphorus-containing monomer has been found to be immiscible with soybean oil and the cationic initiated copolymerization has proven relatively difficult. If so, an improvement in the miscibility of this system should solve the heterogeneity problem. For this reason, we decided to use a different phosphorus-containing monomer, dimethyl-p-vinylbenzylphosphonate (DMVBP). This compound, which is liquid at room temperature and has a lower aromatic content than DPSPO, was obtained from vinylbenzyl chloride and triethyl phosphite following a reported procedure.[12] Polymerization mixtures were prepared as previously described and in all cases homogeneous samples were obtained. BF_3OEt_2/MeOL (3 mol% based on the

total C=C) as initiator was added and a broad exotherm with T_{onset}= 83ºC and T_{max}= 107 ºC was observed in the DSC plot (Figure 1, sample D). From these data and according to previous results,[7] the mixtures were heated at 110ºC. However, again a large number of white particles appeared and a brownish liquid product was recovered, showing that the copolymerization did not produce solid polymers. Further attempts to carry out the copolymerization of the SOY/ DMVBP/ST/DVB system at higher reaction temperatures or increasing the amount of catalyst gave similar results in all cases.
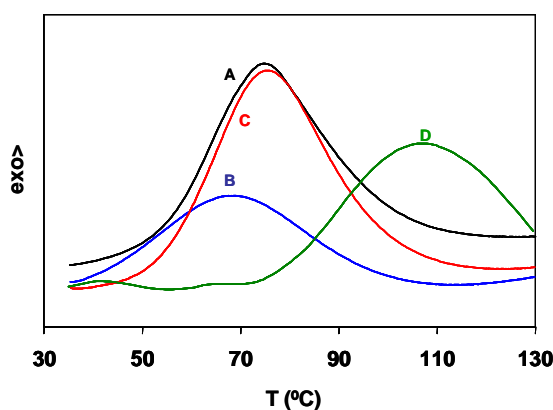
Figure 1. DSC thermograms (10ºC/min) of the curing mixtures.

There are different possible reasons for the heterogeneous nature of these copolymerizations. First, the difference in the reactivity of soybean oil and styrenic monomers, that seems to be increased in presence of DMVBP since homogeneous copolymers are obtained in absence of this monomer. Taking this into account, the white particles should be crosslinked copolymers of the styrene derivatives which contain the highly polar P=O moiety from DMVBP monomer and which would show poor miscibility with soybean oil. In fact,

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when the reaction mixture was extracted with methylene chloride, a soluble fraction was obtained which did not contain styrenic C=C bonds, as revealed by the ^{1}H NMR spectrum. The amount of this soluble fraction ranges from 37 to 43 w %, matching the soybean oil content of the initial polymerization mixture.

Another disadvantage to be considered is that the cationic initiator, BF$_3$OEt$_2$ is a strong Lewis acid that can interact with the basic P=O moieties. The coordination of the catalyst to the phosphoryl groups impedes the polymerization of the internal double bonds of the oil, favouring the homopolymerization of the more reactive styrenic monomers. Moreover, the Lewis acid can promote the hydrolysis of the methoxy groups, leading to the phosphonic acid that would decrease substantially the miscibility of the systems.

To better understand the cause of the heterogeneity in these reaction mixtures, we carried out several experiences. We started by investigating the possible interactions between the catalyst and the phosphoryl moiety. For this purpose, we synthesized dimethylbenzylphosphonate (DMBP) as a model compound containing a P=O group but not a styrenic C=C. When this compound was mixed with the BF$_3$OEt$_2$/MeOL initiator system, an homogeneous solution was obtained. The analysis by ^{31}P NMR revealed the presence of two different signals; apart from the singlet at 29,4 ppm, which belongs to the free P=O group of DMBP, a new singlet appeared at 30,3 ppm due to the Lewis acid-base interaction between part of the phosphoryl groups and the initiator, which takes place at room temperature. Another factor causing heterogeneity could be the hydrolysis of the phosphonate groups

during the curing reaction. To determine whether the hydrolysis was taken place, DMBP was mixed with the BF_3OEt_2/MeOL initiator system and heated at 90ºC for 12h. The ^{1}H NMR analysis of the resulting mixture showed that the signals at 3,6 ppm, attributed to the methoxy groups, remained unaltered, as well as the signals corresponding to the P=O in the ^{31}P NMR spectrum, which still appeared at 29,4 and 30,3 ppm. These results confirm that the hydrolysis of the phosphonate groups does not take place and that the acid-base Lewis complex is stable at high temperatures. To check that the coordinated catalyst is able to initiate the polymerization of the styrenic monomers, the same experiences were carried out using the DMVBP monomer. At room temperature, two signals corresponding to the initial monomer and the coordinated species appear in the ^{31}P NMR spectrum (29.9 and 32.7 ppm, respectively). When heated at 90ºC for 2 h, the polymerization takes place as confirmed by the appearance of the polymer backbone signals between 1,2 and 2,0 ppm and the dissapearance of the vinyl signals at 5,0, 5,6 and 6,5 ppm in the ^{1}H NMR spectrum of the final material.

This indicates that the acid-base Lewis complex gives the active species for the cationic polymerization. In a similar way, the cationic copolymerization between DMVBP, ST and DVB takes place using a 3 mol% of BF_3OEt_2/MeOL.

From the above discussion, it can be concluded that in the SOY/DMVBP/ST/DVB systems the styrenic monomers are first copolymerized giving the observed particles, which precipitate from the polymerization mixture and are not able to serve as active polymerization centers. Subsequently, the most part of the styrenic monomers are consumed before copolymerization with the oil takes place, and oil homopolymerization

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happens solely on the residual solution. In this way, the difference in the reactivities between the oil and the styrenic monomers under the above described reaction conditions is the main reason for the heterogeneous copolymerization reactions.

Several attempts to obtain SOY/DMVBP/ST/DVB homogeneous materials were carried out. We previously described the cationic copolymerization of soybean oil, styrene and divinylbenzene under microwave irradiation using BF_3OEt_2/MeOL as initiator, and a comparison with conventional heating showed great enhancement of reaction rates.[15] In this way, the cationic copolymerization of the system was carried out under microwave irradiation using different power inputs and reaction times. Solid materials of extremely fragile nature and poor mechanical integrity were obtained in all cases, which contained high loadings of soluble fractions. Finally, we attempted to use other Lewis acid initiators as HBF_4 or $Yb(OTf)_3$ to carry out the polymerization, but in any case improvements on the homogeneity of the materials were observed.

In view of these disappointing results, the development of a phosphorus-containing oil miscible compound of similar reactivity to the oil was key in order to incorporate a reactive phosphorus derivative to the soybean oil copolymers. For this purpose, we chose the olefin cross-metathesis as a synthetic method to chemically attach a phosphorus moiety to a vegetable oil derivative. The olefin metathesis with oleochemicals allows for a versatile introduction of many different functional groups taking advantage of the double bond functionality of fatty-acid derivatives. We carried out the metathesis of methyl 10-undecenoate (MU), which can be obtained from

pyrolysis of castor oil, and DMVBP with first (C1) and second (C2) generation Grubbs catalysts.

Olefin cross metathesis is a convenient route to functionalized and higher olefins from simple alkene precursors.[16] The cross metathesis of methyl 10-undecenoate with terminal[17] or internal olefins[18] has been described. Due to the higher reactivity of terminal olefins, if compared to the internal double bonds, even C1 is able to catalyze the cross-metathesis of this compound although the self-metathesis product dominates. Better results are described for C2 with almost full conversion for lower catalyst loading without large amounts of by-products. On the other hand, styrenes represent one of the classes of olefins used in cross-metathesis because of the slow dimerization of styrene to stilbene, allowing for selective cross coupling. Thus, the cross-metathesis products are usually obtained in moderate yields and only terminal olefins are employable in cross-metathesis with C1. However, the N-heterocyclic carbene-based ruthenium complex C2 efficiently catalyzes the cross coupling of styrenes with a variety of substituted olefins.[19]

We examined the reaction of MU with DMVBP (Scheme 2) using C1 and C2 and CH_2Cl_2 as solvent at reflux temperature for 12 h and Table 1 summarizes the results. As can be seen, lower conversions in a clean reaction without large amounts of self-metathesis were obtained when using C1. When C2 was employed significant higher conversion was observed, but the yield of self-metathesis also significantly increased. The highest cross-metathesis yield was obtained using stoichiometric amounts of MU and DMVBP and 2% of C2. The cross-metathesis product (MU-DMVBP) was characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Characteristic signals

for C=C double bond at 6.10-6.19 and 6.32 ppm in the ^{1}H NMR spectrum, and at 129.42 and 131.50 ppm in the ^{13}C NMR spectrum can be seen.

MU-DMVBP was mixed with soybean oil, ST and DVB with the compositions shown in table 2. The amount of DVB was kept constant and the amounts of MU-DMVBP, ST and SOY were varied to obtain thermosets with a phosphorus content of 1 w%. In all cases, homogeneous mixtures were obtained and the curing reaction were studied by dynamic DSC (Figure 1).

The plots showed a broad exotherm that shifted at slightly lower temperatures when ST was substituted by MU-DMVBP (sample C). From the DSC data, curing and postcuring conditions were established as 12h at 80°C, 24h at 140°C and 12h at 160°C.
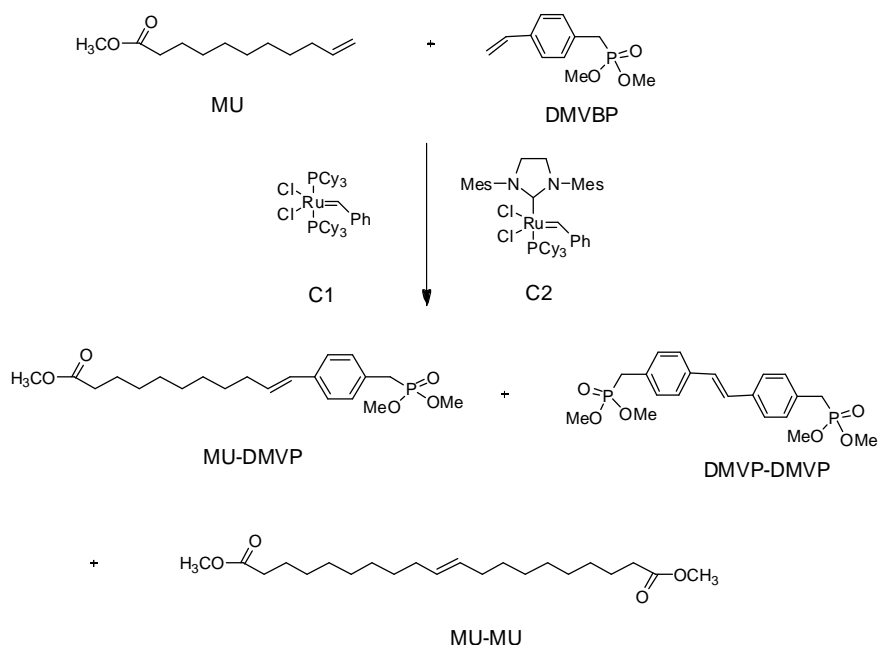
Scheme 2. Reaction of MU wiyh DMVBP using C1 and C2 catalyst.

Table 1. Self and cross-metathesis results of the methyl 10-undecenoate (MU) with DMVBP (T= 45ºC, reactions performed with 0,5 g in CH2Cl2 for 12h)

Catalyst (mol %)	Molar ratio (DEVBP/MU)	C (%)[c]	CM (%)[d]	SM (%)[e]
C1 (2)	2.0	36.8	28.5	8.3
C1 (2)	2.0[a]	46.4	38.0	8.4
C1 (2)	1.4[b]	55.4	43.9	11.5
C1 (2)	1.0	53.7	38.0	15.7
C2 (1)	1.0[a]	70.9	42.6	28.3
C2 (2)	1.0[a]	90.4	60.4	30.0
C2(2)	2.0	98.6	40.6	58.0

a Without solvent.
b 0.4 mol of MU was added after 12h of reaction.
c Conversion of MU in % (RMN).
d Yield of cross-metathesis products in% (RMN estimate).
e % Self-metathesis products of all products (RMN estimate).

The obtained copolymers were obtained in essentially quantitative yields and appeared as dark-brown rubbery materials at room temperature ranging from tough to very soft rubbers. The composition of the copolymers was studied by analysing the results of overnight soxhlet extractions with methylene chloride as a refluxing solvent. A 59 w% of insoluble materials was retained from the bulk materials when ST was substituted by MU-DMVBP (sample B), which contains a less reactive C-C double bond. A higher amount of insoluble fraction was obtained when part of SOY was substituted by MU-DMVBP (sample C), according to a higher reactivity of this compound. The soluble fractions were characterized by ^{1}H NMR spectroscopy. The presence of signals at 3.6 and 3.1 ppm, corresponding to the CH_3-O and CH_2-P protons, and a broad signal centered at 7.0 ppm

corresponding to the aromatic and C=C protons of MU-DMVBP confirmed the presence of this compound. Moreover, signals at 4.2, 2.7 and 2.0 ppm, attributable to the soybean oil could be observed. These results indicated that the soluble fractions were composed of oligomeric fractions and unreacted moieties. The P content of the soluble fraction (Table 2) was calculated from the ^{31}P NMR spectra using triphenylphosphine as an internal standard (-4.9 ppm) by integrating the signal at 29.4 ppm. As can be seen, the reactive phosphorus-containing flame retardant was mainly incorporated into the network and retained in the insoluble fraction

Table 2. Copolymerization mixtures, curing data and composition of the copolymers

| Sample | P wt % | Molar ratio | | | | T_{onset} (ºC) | T_{max} (ºC) | Soluble fraction (%) | Insoluble fraction (%) | P Soluble fraction (%) |
		SOY	MU-DMVBP	ST	DVB					
A	-	1.00	-	6.00	2.25	52	74	8	92	-
B	1	1.00	0.69	5.30	2.25	41	68	41	59	0.5
C	1	0.83	0.75	6.00	2.25	54	75	22	78	0.2

DMA was used to investigate the dynamic mechanical behaviour of the copolymers. Figure 2 shows the storage moduli and the Tan δ values of the samples. The storage modulus of the phosphorus containing copolymers is lower than the one of the phosphorus free sample at temperatures higher than the temperature range corresponding to the primary relaxation process.

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Moreover, the crosslinking density of sample A is much higher than those of the phosphorus-containing samples, due to their higher soluble fraction content. From the Tan δ plots, the presence of a shoulder indicates that the copolymers have two glass transition temperatures which merge into a very broad transition.
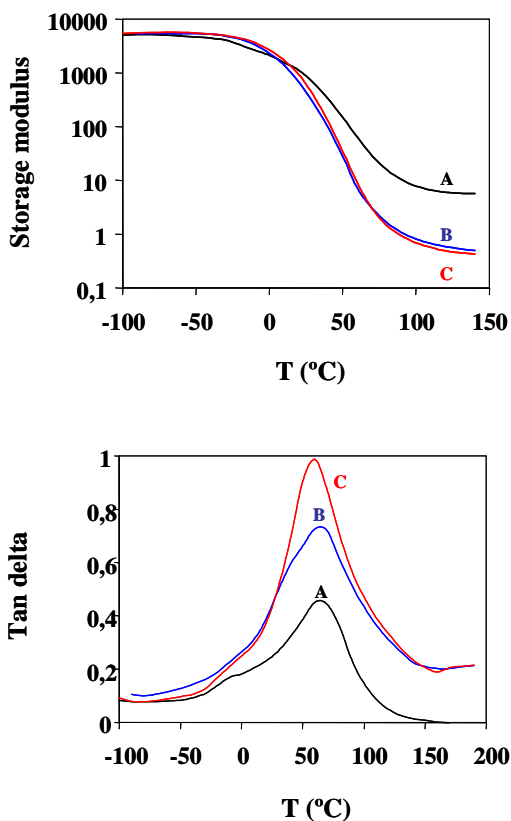

Figure 2. Storage Modulus and Tan delta of the copolymers.

The copolymers appear to be complex heterogeneous systems composed of hard aromatic-rich phases and soft oil-rich phases, with a certain amount of oligomers that act as plasticizers. The high temperature transition (around

60ºC) corresponds to the glass transition temperature of the plasticized aromatic-rich phase, while the low temperature transition (-10ºC) is attributed to the plasticized oil-rich phase. The height of the Tan δ peaks increases for samples B and C, according to a lower crosslinking density.

The thermal stability of the copolymers was analysed by TGA (Figure 3). Both in air and in nitrogen atmospheres, the decomposition temperatures ($T_{5\%}$) for the phosphorus containing copolymers are lower than for the phosphorus free resin (Table 3).
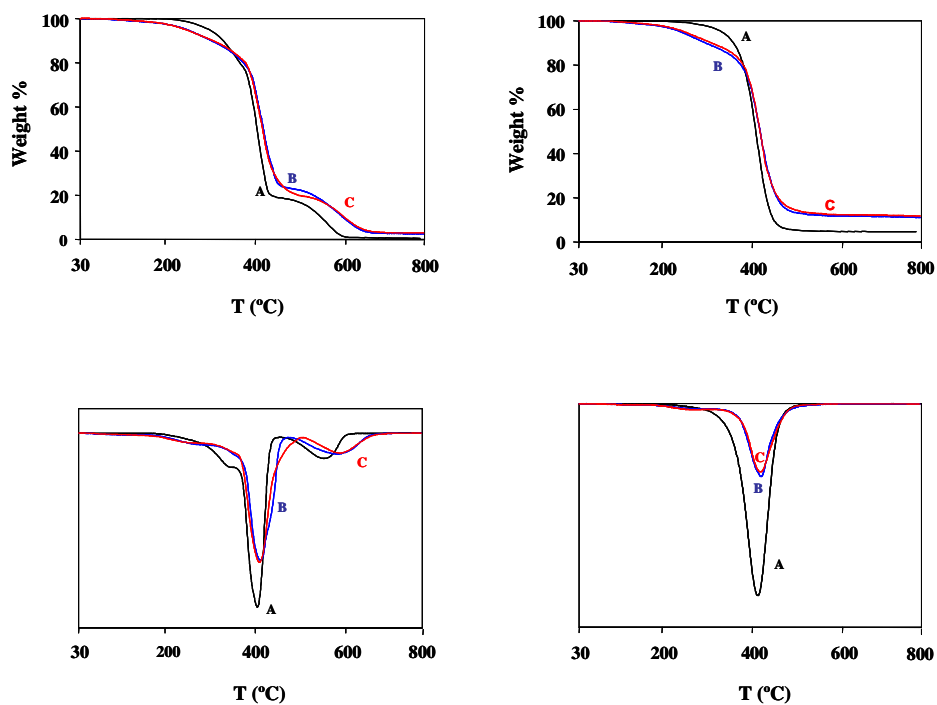
Figure 3. TGA plots (10ºC/min) and first derivative curves of the copolymers.

This weight loss at low temperatures should be attributed to the decomposition of unreacted monomers and low molecular weight oligomers. Under nitrogen atmosphere the degradation takes place in one step and in air a three stage weight loss can be seen for the three samples. The first stage is attributed to the decomposition of soluble fractions, while the second corresponds to the crosslinked polymer degradation that takes place at a faster rate.

The thermooxidative degradation is observed at temperatures higher than 500ºC and takes place at a lower weight loss rate and higher temperatures for the phosphorus containing polymers.

Table 3. Thermal properties of the copolymers

| Sample | Tg (ºC)[a] | Nitrogen | | | Air | | | LOI |
		$T_{5\%}$ (ºC)[b]	T_{max} (ºC)[c]	Yield$_{800}$ (ºC)[d]	$T_{5\%}$ (ºC)[b]	T_{max} (ºC)[c]	Yield$_{800}$ (ºC)[d]	
A	62	355	432	5	308	362, 434, 582	1	19.2
B	66	258	438	11	267	272, 437, 608	3	23.1
C	59	266	438	12	265	298, 435, 613	3	24.0

a Glass transition temperatures are calculated from the maxima of Tanδ curves
b Temperature of 5% weight loss
c Temperatures of the maximum weight loss rate
d Char yield at 800ºC

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This behaviour is in accordance with the mechanism of improved fire performance via phosphorus modification. In this retarded-degradation phenomenon, the phosphorus groups form an insulating protective layer, which prevents the combustible gases from transferring to the surface of the materials, increases the thermal stability at higher temperatures and improves the fire resistance. Char yields under air and nitrogen increase slightly for the phosphorus containing copolymers.

To test the fire resistance, LOI measurements were carried out. LOI values increase from 19.2 for the phosphorus free system to 23.1 and 24.0 for copolymers B and C, according to the expected behaviour for fire retarded phosphorus containing materials. Previous work on silicon[7] and boron[20] containing soybean oil copolymers showed similar LOI values for similar heteroatom percentages (22.6 for Si and 23.7 for B). These results show that the phosphorus-containing copolymers no longer burn in ambient air without complementary oxygen, suggesting that these biobased materials are very interesting for applications that require fire resistance.

CONCLUSIONS

To extend the application possibilities of vegetable oil-based thermosets by improving their flame retardance we investigated the influence of two phosphorus containing styrene derivatives (dimethyl-p-vinylbenzylphosphonate (DMVBP) and diphenyl styryl phosphine oxide (DPSPO)) in the cationic copolymerization of soybean oil, styrene and divinylbenzene, obtaining heterogeneous systems in both cases. We carried

out the cross-metathesis reaction of methyl 10-undecenoate and DMVBP to attach the phosphorus moiety to the vegetable oil derivative and incorporated this reactive phosphorus derivative (MU-DMVBP) to the soybean oil, styrene and divinylbenzene system. The cationic copolymerization has been investigated and thermosets with good mechanical properties have been obtained. Dynamic mechanical analysis indicates that the crosslinking density decreases and no significant differences on the glass transition temperature have been observed. Thermogravimetric analysis shows that the thermal stability decreases and LOI measurements show that the phosphorus-containing copolymers no longer burn in ambient air without complementary oxygen.

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3. *General Conclusions*

CONCLUSIONS

New flame retardant biobased thermosets have been developed from soybean oil, showing that it is possible to exploit renewable resources to manufacture materials with fire retardant properties. These results in more detail are stated below:

- Novel thermosetting copolymers have been prepared by cationic copolymerization of soybean oil, styrene, divinylbenzene and p-trimethylsilylstyrene (SiST) catalyzed by boron trifluoride diethyl etherate, with a silicon content between 1.0 and 7.0 wt%. These silicon-containing copolymers show enhanced fire retardant properties.

- Novel thermosetting copolymers have been prepared by cationic copolymerization of soybean oil, styrene, divinylbenzene and tris(4-vinylphenyl)boroxine (BST) catalyzed by boron trifluoride diethyl etherate, with a boron content between 1.0 to 3.0 wt%. The presence of boron does not change the thermal stability and the incorporation of BST into the polymer matrix results in a notable increase of LOI values.

- The cone calorimetry experiments gave much clearer evidence than LOI measurements that incorporation of Si or B into the soybean oil copolymer resulted in fire retardation. This indicates the formation of a protective layer following ignition, reducing the rate of gas-phase fuel formation. The boron-containing copolymers were found to be the more efficient flame retardants for this system than the silicon-containing copolymers.

- A noticeable acceleration of cationic polymerization rate of soybean oil and cationic copolymerization of soybean oil, styrene and divinylbenzene when performed under microwave irradiation were observed. DMA analysis indicates that the dynamic mechanical behavior of these materials is very similar to that of the copolymers obtained under conventional heating. Moreover, the content and composition of the soluble and insoluble fractions were also similar.

- The influence of two phosphorus-containing styrene derivatives (dimethyl-p-vinylbenzylphosphonate (DMVBP) and diphenyl styryl phosphine oxide (DPSPO)) in the cationic copolymerization of soybean oil, styrene and divinylbenzene was investigated and heterogeneous systems were obtained in both cases. The cross-metathesis reaction of methyl 10-undecenoate and DMVBP was carried out. As a result, the phosphorus moiety was attached to the vegetable oil derivative to obtain a reactive phosphorus derivative (MU-DMVBP) that was added to the soybean oil, styrene and divinylbenzene system. In this way, homogeneus systems were obtained.

4. Apendixes

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APENDIXES

Apendix A. List of abbreviations

^{1}H, ^{13}C and ^{31}P-NMR	Proton, carbon and phosphorus nuclear magnetic resonance
ADMET	Acyclic diene metathesis
ARHE	Average rate of heat emission
BAD	tris-(phenylboroxine)
BFE	Boron trifluoride
BF$_3$·OEt$_2$	Boron trifluoride diethyl etherate complex
BST	Tris(4-vinylphenyl)boroxine
CM	Cross-metathesis
DMBP	Dimethylbenzylphosphonate
DMTA	Dynamomechanical thermal analysis
DMVBP	Dimethyl-p-vinylbenzylphosphonate
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DPSPO	Diphenyl styryl phosphine oxide
DSC	Differential scanning calorimetry
DVB	Divinylbenzene
FIGRA	Fire growth rate index
FR	Flame retardant
FTIR/ATR	Fourier transform infrared spectroscopy/

	Attenuatted-Total-Reflection
GC/MS	Gas chromatography coupled with mass Spectrometry
GPC	Gel permeation chromatography
hr-MAS NMR	High resolution magic angle spinning nuclear magnetic resonance
HRR	Heat Release Rate
LOI	Limiting oxygen index
MARHE	Maximum average rate of heat emission
MAS NMR	Magic angle spinning nuclear magnetic Resonance
MeOL	Methyl oleate
MLR	Mass Loss Rate
M_n	Number average molecular weight
MU	Methyl-10-Undecenoate
M_w	Weight average molecular weight
NHC	N-heterocyclic carbene
OI	Oxygen index
PHRR	Peak heat release rate
POSS	Polyhedral oligomeric silsesquioxane
RCM	Ring Closing Metathesis
ROM	Ring Opening Metathesis
ROMP	Ring Opening Metathesis Polymerization

UNIVERSITAT ROVIRA I VIRGILI
SOYBEAN OIL BASED COPOLYMERS CONTAINING SILICON, BORON OR PHOSPHORUS: POLYMERIZATION,
CHARACTERIZATION AND FIRE RETARDANCE PROPERTIES.
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ISBN:978-84-693-1532-3/DL:T-649-2010

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SiAD	1,3-diphenyl-1,1,3,3-tetramethyldisiloxane
SiST	4-trimethylsilylstyrene
ST	Styrene
SOY	Soybean oil
Tan δ	Loss factor
$T_{10\% \text{ loss}}$	Temperature of 10 % weight loss
$T_{5\% \text{ loss}}$	Temperature of 5 % weight loss
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
THR	Total Heat Release
TLC	Thin layer chromatography
T_{max}	Temperature of maximum weight loss
TMS	Tetramethylsilane
TTI	Time to ignition
UL-94	Standard applied by de American Underwriters Laboratories for testig the flammability
VPB	4-vinylphenyl boronic acid

Apendix B. List of publications

- Silicon-Containing Soybean-Oil-Copolymers. Synthesis and Properties.
  Sacristán, M.; Ronda, J.C.; Galià, M.; Cádiz, V. Biomacromolecules 2009, 10, 2678-2685.

- Rapid Soybean Oil Copolymers Synthesis by Microwave-Assisted Cationic Polymerization
  Sacristán, M.; Ronda, J.C.; Galià, M.; Cádiz, V Macromol Chem and Phys in press.

- Effects on the Flame Retardancy of Boron-Containing Soybean-Oil Based Copolymers
  Sacristán, M.; Ronda, J.C.; Galià, M.; Cádiz, V Polym Degrad Stab, submitted.

- Cone Calorimetry Studies of Fire Retardant Soybean-Oil-Based Copolymers Containing Silicon or Boron: comparison of additive and reactive approaches
  Sacristán, M.; Ronda, J.C.; Galià, M.; Cádiz, V. Polym Degrad Stab, submitted.

- Approaches to phosphorus-containing soybean oil copolymers. Cross-metathesis of fatty acid derivatives as an alternative to phosphorus-containing reactive flame retardants.
  Sacristán, M.; Ronda, J.C.; Galià, M.; Cádiz, V. Polym Degrad Stab, submitted.

Apendix C. Stages and meeting contributions

Stages

Three months stay (1st February - 1st May 2009) at the University of Central Lancashire, Faculty of Science and Technology, Preston (United Kingdom) under the supervision of Prof. Dr. Richard Hull.

Meeting contributions

- Flame Retarding Effects of Silicon in New Soybean-Based Copolymers.
  M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz.
  Poster.
  11th European Meeting on Fire Retardant Polymers, Bolton, Manchester (UK), 03-06 July, 2007.

- Polímeros Retardantes a la Llama Derivados de Aceite de Soja.
  M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz.
  Poster.
  X Reunión del Grupo Especializado de Polímeros (RSEQ y RSEF), Sevilla (Spain), 6-20 September, 2007.

- New Soybean-Based Thermosets.

  M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz.

  Poster.

  Fire Retardant Technologies (RSC), Preston (UK), 21-23 April, 2009.

- Towards New Phosphorus-Containing Vegetable Oil Based Copolymers as Flame Retardant Materials.

  M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz.

  Poster.

  Frontiers in Polymer Science International Symposium, Mainz (Germany), 7-9 June, 2009.

- Towards New Phosphorus-Containing Vegetable Oil Based Copolymers as Flame Retardant Materials.

  M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz.

  Poster.

  XI Reunión del Grupo Especializado de Polímeros (RSEQ y RSEF), Valladolid (Spain), 20-24 September, 2009.