Synthesis and properties of boron-containing soybean oil based thermosetting 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. The thermal degradation mechanism was studied and the thermal, dynamomechanical and flame retardant properties of these materials were examined. Thermosets with glass transition temperatures ranging from 43 to 60 °C, which are thermally stable below 350 °C 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.

1. Introduction

The replacement of petroleum-based raw materials by renewable resources constitutes a major contemporary challenge in terms of both economical and environmental aspects [1,2]. 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 [3]. Recently there have been many attempts to convert vegetable oils and fatty acids to useful polymers [4]. 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 [5] and its cationic homopolymerization is relatively difficult [6]. 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

[7] or from acrylated epoxidized natural oils and styrene have been proposed [8].

Even 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 nontoxic characteristics. Vegetable 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 are 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 of new environmentally friendly flame retardant polymeric materials. Phosphorus, silicon and boron-containing polymers are well recognized for their flame retardant properties, [9] and they are increasingly becoming more popular than their halogen counterparts, as they generally give off nontoxic combustion products [10]. 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 [11].

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

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[12]. The use of borates in enhancing the flame retardancy of polymeric materials was reported earlier in the 20th century [13]. 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 [14]. 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 [15]. 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 [16,17], 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 [18] 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 [19,20]. Moreover the copolymerization of 4-vinylphenyl boronic acid with styrene-divinylbenzene mixtures and other unsaturated monomers have been well described [21].

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 (Scheme 1). The polymerization behaviour, structure, thermal stability and mechanical and flame retardant properties of the resulting materials have been studied. Moreover, the thermal degradation mechanism has been investigated and compared with that of the soybean oil copolymers obtained by adding boron-containing fire retardant additives.

2. Experimental section

2.1. 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 linoleic (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 butyllithium (0.6 M in hexane) were supplied 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 [22] and purified by crystallization in water. Yield: 61%, mp: 185–189 °C. Tris(4-vinylphenyl) boroxine (BST) was obtained by removing water azeotropically with toluene following a reported procedure [23]. Yield: 92%, mp: 194–196 °C. The soybean oil copolymer obtained by adding tris-(phenylboroxine) as a fire retardant additive (3% boron content) was obtained as previously described [24].

Soybean oil
(SOY)

Styrene
(St)

Divinylbenzene
(DVB)

4-vinylphenyl boronic acid
(VPB)

tris(4-vinylphenyl)boroxine
(BST)
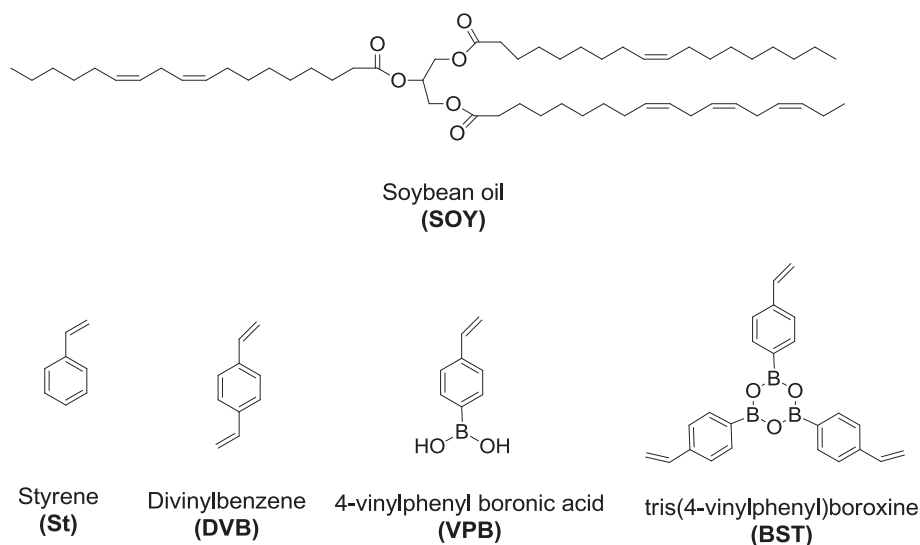
Scheme 1. Monomers used in the copolymerizations.

2.2. Cationic copolymerization

The following reaction procedure was usually employed, unless otherwise stated in the text. The desired amounts of tris(4-vinyl-phenyl)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 12 h at the appropriate temperatures: at 60 °C for SSD, 70 °C for SSDB1 and 90 °C for SSDB2 and SSDB3. In all cases, 24 h of post-curing at 160 °C was applied.

2.3. 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.

2.4. 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 ^1H and ^{11}B NMR spectra were recorded at room temperature on a Varian Gemini 400-MHz spectrometer (400 MHz for ^1H 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$_2$D$_2$Cl$_4$ (TCE-d$_2$) were used as solvents. Copolymer insoluble fractions were swollen in DMSO-d$_6$ or TCE-d$_2$. ^1H HR-MAS NMR spectra were recorded on a Bruker 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 27 °C. 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 ^1H 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 10 °C/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 900 °C under air atmosphere for 5 h. 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 [25]. Degradation studies were carried out in a Carbolite TZF 12/38/400 oven connected to a condenser cooled by liquid nitrogen. GC-MS measurements were carried out using an HP 6890 gas chromatograph with an Ultra 2 capillary column (crosslinked 5% PH ME siloxane) and an HP 5973 mass detector.

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 100 °C at a heating rate of 3 °C/min and a fixed frequency of 1 Hz.

LOI measurements (LOI ISO 4589) were performed on a Stanton Redcroft FTA flammability unit provided with an Oxygen Analyzer. Sample sizes measured $100 \times 5 \times 4$ mm^3 and were prepared by moulding.

3. 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 [6]. In our case, the initiator system was obtained by mixing boron trifluoride diethyl etherate 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 [6]. 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 [22]. 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.

It is well known that boronic acids, specially the aromatic ones, undergo loss of water under very mild conditions leading to tris(aryl)boroxines [26,27]. 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. 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) [28], and by ^1H NMR (absence of the signals corresponding to the hydroxyl groups at 7.2 ppm).

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

Table 1
Molar composition, curing behaviour and curing conditions of the copolymerization mixtures (mols BF$_3$.OEt$_2$: 0.41).

System	% B	SOY	St	BST	DVB	T_{onset}[a] °C	T_{max}[b] °C	Curing[c, d] T (°C)
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	118	145	90

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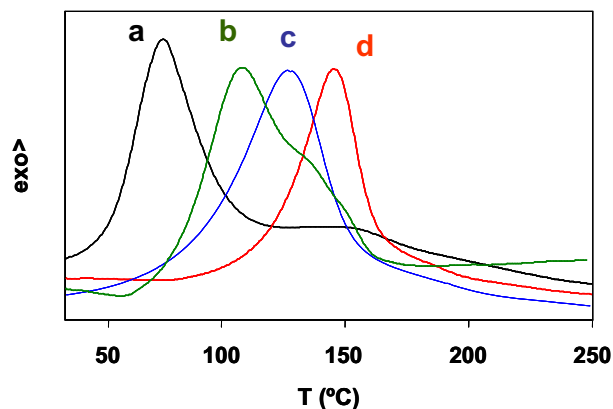[d] Post-curing at 160 °C for 24 h.

Fig. 1. DSC plots (10 °C/min) of curing mixtures (a) SSD, (b) SSDB1, (c) SSDB2 and (d) SSDB3.

1%, 2% and 3% (w/w) of boron were obtained. The amount of catalyst (BF$_3$OEt$_2$/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.

Prior to the preparation of the thermosets, the curing reaction behaviour was studied by dynamic DSC (Fig. 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 52 °C to 118 °C. 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, 12 h for the curing process and 24 h at 160 °C for the post-curing one were selected. Higher temperatures or longer times did not increase the crosslinked fraction in a significant way.

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 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 24 h 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. The soluble fractions were characterized by ^{1}H NMR spectroscopy (SSD3, Fig. 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$_2$O$_3$ residue at 900 °C by thermogravimetric analysis.

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 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. Fig. 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

Table 2
Composition of the copolymers.

Sample	Feed composition (w%)	Soluble fraction			Insoluble fraction		
	B content	Aromatic fraction	Yield (w %)[a]	Aromatic frac. (%)[b]	Yield (w %)[a]	B content (%)[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$_2$O$_3$ residue after pyrolysis at 900 °C 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.
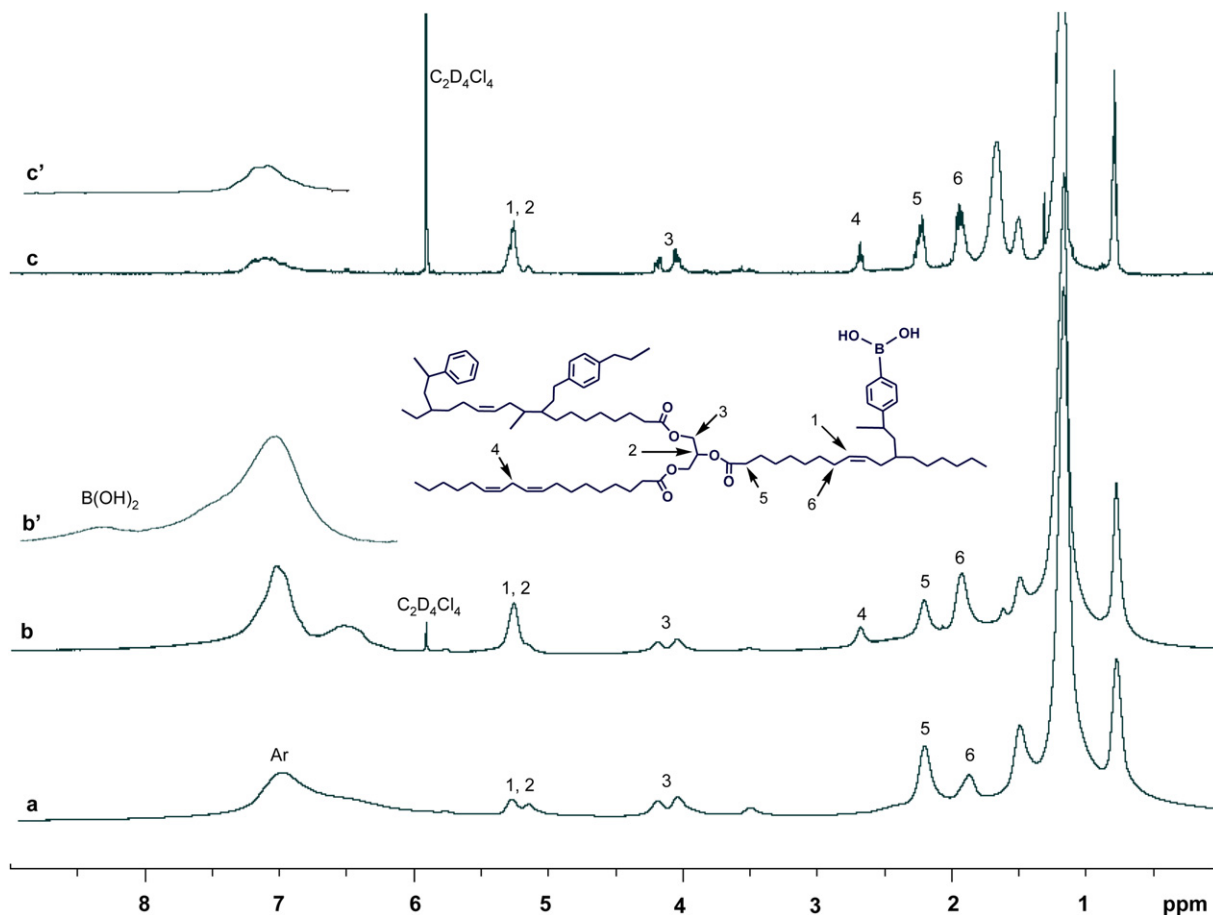
Fig. 2. ^{1}H HR-MAS NMR spectra of the insoluble fractions of samples SSD (a) and SSDB3 (b) swollen in TCE-d$_2$ and b′ SSDB3 swollen in DMSO-d$_6$. ^{1}H NMR spectra of the soluble SSDB3 fraction recorded in TCE-d$_2$ (c) and in DMSO-d$_6$ (c′).

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 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 (Fig. 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 (Fig. 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 (Fig. 2c′).

DMA has been used to investigate the dynamic mechanical behaviour of the copolymers. Fig. 3 shows the storage moduli and the tan δ values of the samples with different boron content. At temperatures below −40 °C 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 −30–100 °C, 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
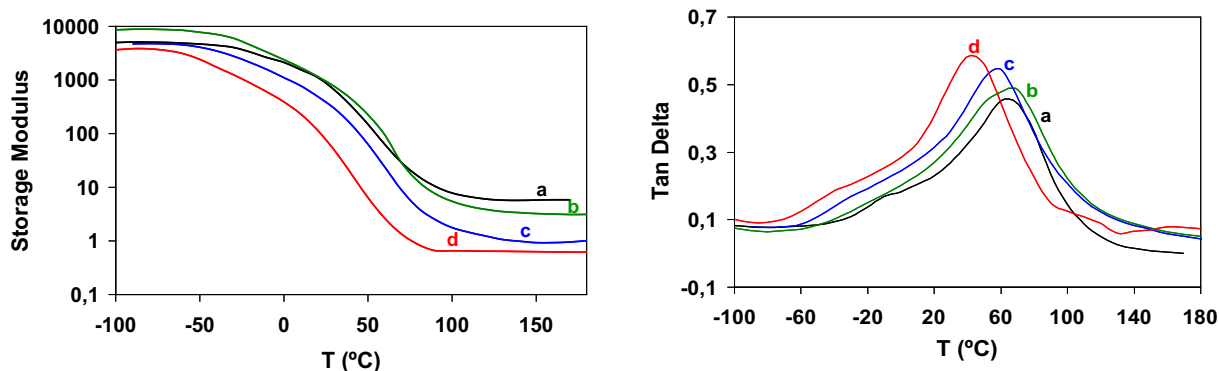
Fig. 3. Storage modulus and loss factor of the copolymers.

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 50 °C 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 [29]. 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. 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 Fig. 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 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 a plasticizers. The high temperature transition (62°–43 °C) corresponds to the glass transition temperature of the plasticized aromatic rich phase, while the low temperature transition (−10 °C to −41 °C) is attributed to the oil rich phase. 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. Fig. 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 300 °C but a slight drifting starting around 100 °C 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 [25]. The onset temperatures in air atmosphere are lower than in nitrogen, mainly due to the mechanism of peroxidation that takes place when oxygen is present.

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 800 °C, indicating that all systems exhibit quite similar thermal behaviour. In air, three weight loss stages can be seen. The first stage around 360 °C can be due to decomposition of soluble components, while the second stage around 400–450 °C corresponds to the crosslinked polymer degradation that takes place at a faster rate. The third stage is observed at temperatures around 600 °C and corresponds to the thermooxidative degradation. 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 [30], these polymers were expected to have good flame retardant properties.

To further investigate the thermal degradation mechanism, samples were heated in an oven at 280 °C for 2 h with air as purge gas. To compare, a soybean oil, St and DVB copolymer containing tris-(phenylboroxine) as a fire retardant additive (3% boron content) was also investigated.

The degradation temperature was selected from dynamic TGA data and the time at which no weight loss was detected at 280 °C in an isothermal TGA experiment was selected as the degradation time.

Table 3
Thermal properties of the copolymers.

Sample	ν_e (mol/m^3)[a]	Nitrogen				Air			
		Tg (°C)[b]	$T_{10\%}$ (°C)[c]	T_{max} (°C)[d]	Yield 800 °C (%)[e]	$T_{10\%}$ (°C)[c]	T_{max} (°C)[d]	Yield 800 °C (%)[e]	LOI
SSD	659	62	378	432	5	349	362, 434, 582	0	19.2
SSDB1	417	60	357	421	8	351	360, 425, 584	7	23.7
SSDB2	155	51	355	428	13	344	362, 430, 576	10	24.6
SSDB3	70	43	359	435	18	332	365, 436, 560	17	25.6

[a] Crosslinking densities calculated 50 °C 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.
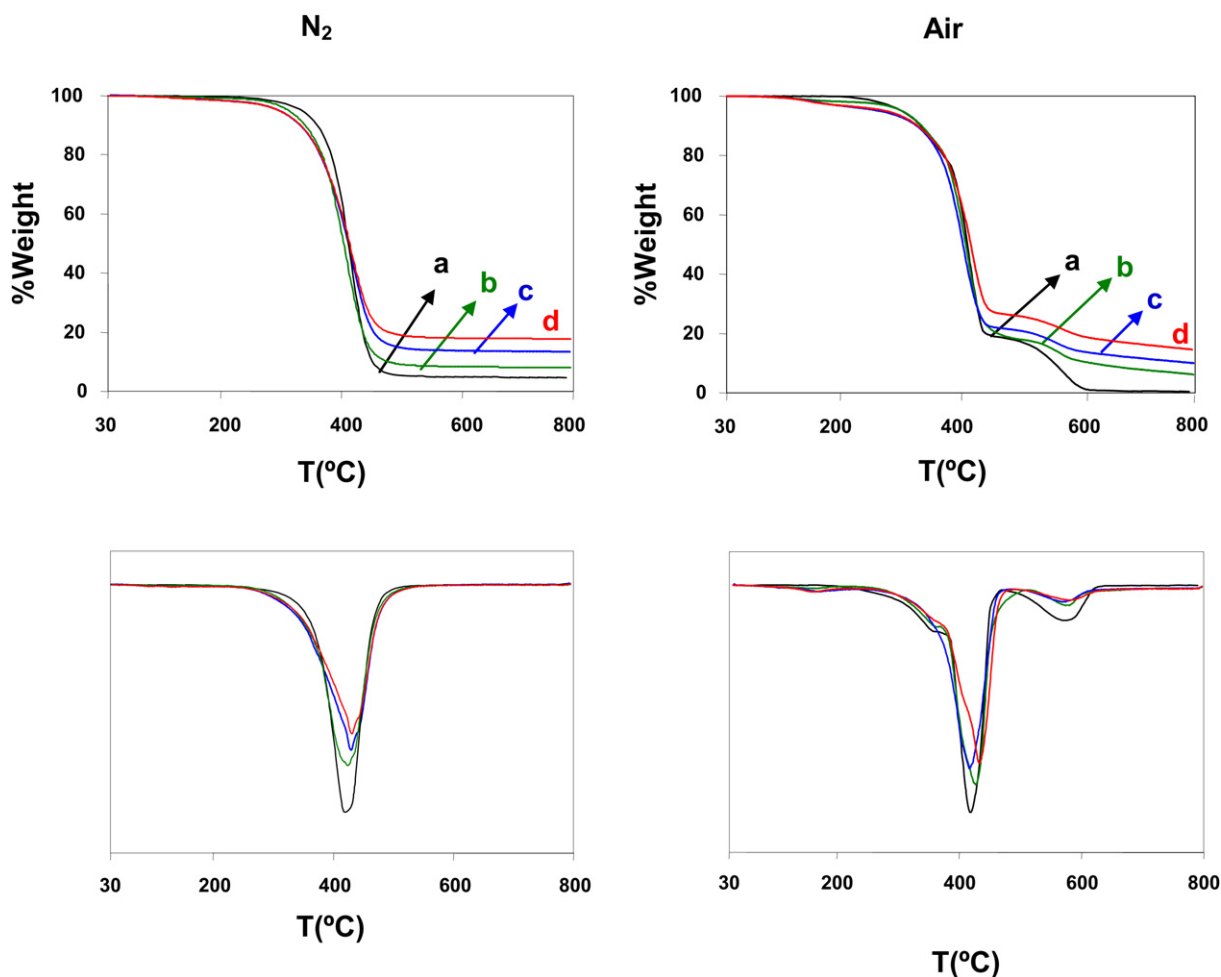[e] Char yield at 800 °C.

N₂

Air

Fig. 4. TGA plots (10 °C/min) and first derivative curves of the copolymers.

Volatile products were trapped as an oily residue plus a colorless liquid fraction, which was essentially water. As expected, the amount of this fraction increases as the boron content does, as well as the amount of the oily residues (Table 4). The analysis of the viscous residues by GC/MS shows the presence of various aliphatic and aromatic species (Scheme 2). No significative differences could be observed among boron free and boron-containing samples, either in reactive or additive form. The mixture contains the expected degradation products for a soybean oil based polymer: fatty acids, fatty esters, alkanes and alkenes [31]. Moreover, aromatic products as styrene, benzaldehyde, ethylbenzaldehyde, ethyl styrene, diethyl styrene and diphenyl butane and its isomers are expected from a styrene/divinylbenzene containing polymers [32,33]. The presence of long chain alkyl and alkenyl benzene derivatives confirms the effective copolymerization of oil and styrene or divinylbenzene. The most noticeable feature of these analyses is that no boron-containing species were detected, thus showing that at low temperatures it remains in the solid residue. The amount of the solid residues decreases as the boron content increases, and no significant differences are observed among the reactive and the additive approach. The boron content of these residues, obtained by TGA, was found to

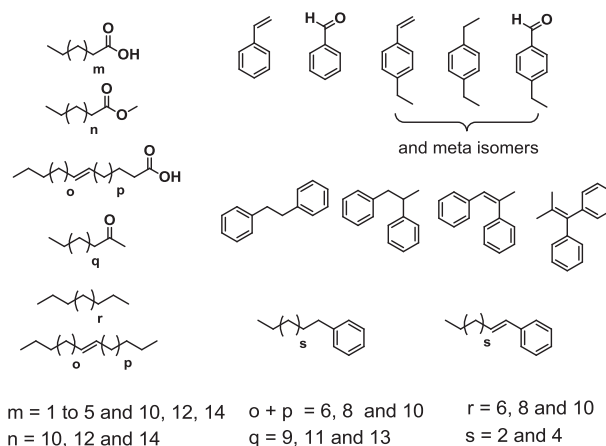**Table 4**
Thermal degradation studies.

Sample	Yield (%)[a]	B (%)[b]	B(%)[c]	Volatiles (%)[d]
SSD	93.8	–	–	2.6
SSDB1	86.9	1.15	1.55	7.6
SSDB2	85.2	2.30	2.42	8.6
SSDB3	82.9	3.61	3.64	10.2
SSDBA3	80.5	3.72	3.80	9.9

[a] Residue after heating at 280 °C for 2 h.
[b] Theoretical percentage of B.
[c] Experimental B percentage.
[d] Condensed volatiles.

and meta isomers

m = 1 to 5 and 10, 12, 14   o + p = 6, 8 and 10   r = 6, 8 and 10
n = 10, 12 and 14   q = 9, 11 and 13   s = 2 and 4

Scheme 2. Products identified by GC-MS in the volatile pyrolisis fraction of SSD, SSDB1, SSDB2, SSDB3 and SSDBA3.

be slightly higher than the one calculated assuming that no boron species are evolved. These observances seem to be in accordance with a phase condensed flame retardance mechanism.

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 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 [16,19] for boron-containing linear styrenic polymers that boron contents higher that 3% are needed to get small increases in the LOI values. 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. Previous work on silicon-containing soybean oil copolymers showed similar LOI values for similar heteroatom percentages [11]. The boron-containing copolymers were found to be more efficient flame retardants for this system than were the silicon-containing, as has been observed by cone calorimetry studies [24].

4. Conclusion

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 and 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. Results from the thermal degradation studies seem to be in accordance with a phase condensed flame retardance mechanism. The incorporation of BST into the polymer matrix results in a notable increase of LOI values, which suggest that these boron-containing biobased materials are interesting for applications that require fire resistance.

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