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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.

1. 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

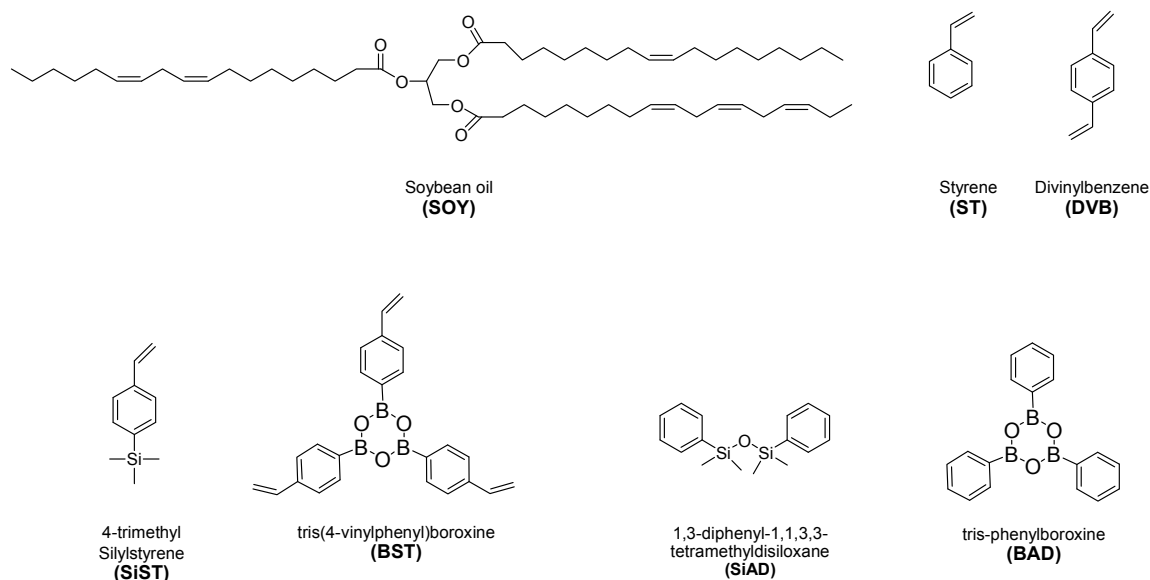
compostability and biodegradability of the resultant polymer materials at their end of life.

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 siliceous 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 CO₂. [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).



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]

2. Experimental

2.1 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 ($\text{BF}_3\cdot\text{OEt}_2$) (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.

2.2 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 mm³ aluminium moulds. Curing conditions are shown in Table1.

Table 1. Molar ratio of the different copolymers synthesised (DVB:2.25, MeOL:0.36; BF₃OEt₂: 0.41) and curing conditions.

Molar ratio									Curing conditions			
System	SOY	ST	SiST	SiAD	BST	BAD	%Si	%B	t (h)	T (°C)	t (h)	T (°C)
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

2.3 LOI measurements (LOI ISO 4589)[14]

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

2.4 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 °C at a constant heating rate of 10 °C/min.

2.5 Cone calorimetry

The combustion behaviour of the polymer plaques, $100 \times 100 \times 2$ 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.

2.6 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 100°C at a heating rate of 3°C/min and a fixed frequency of 1 Hz.

3. Results and discussion

3.1 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 ease 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).

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. The difficulty in synthesizing large quantities of samples restricted the number of cone calorimeter tests to duplicates in each case. Averages are presented as to an appropriate number of significant figures.

Table 2. LOI and cone calorimetric data measured with an irradiance of 35 kW/m².

Samples	LOI	TTI (s)	PHRR (kW/m²)	THR (MJ/m²)	FIGRA (KW/m²s)	MARHE (KW/m²)	Total smoke release (Kw/m²)
C	19.2	25	510	36.7	7.3	235	740
CSiR	28.6	37	620	43.8	8.8	244	1190
CSiA	26.0	18	930	33.7	18.5	412	1400
CBR	25.6	44	410	32.5	3.7	178	370
CBA	25.2	52	530	32.8	6.6	278	990

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.

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 value similar to the heteroatom free system. 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.

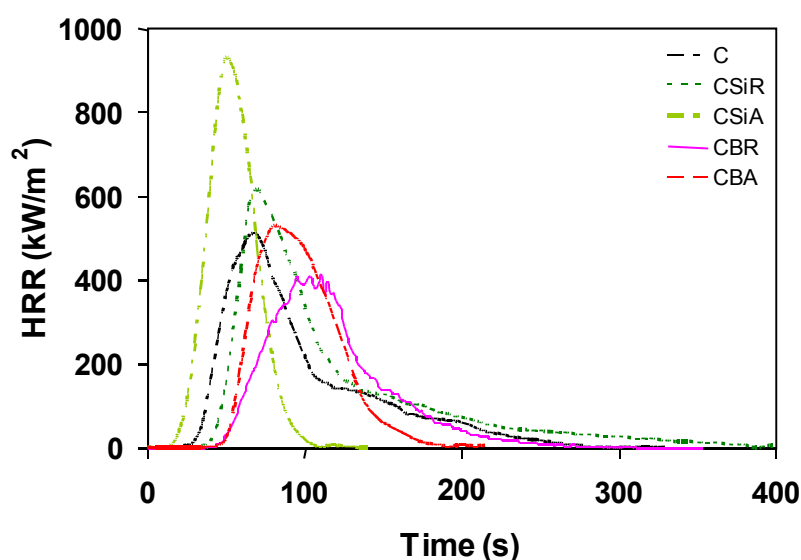


Figure 1. HRR vs. time for the different copolymers synthesised.

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%.

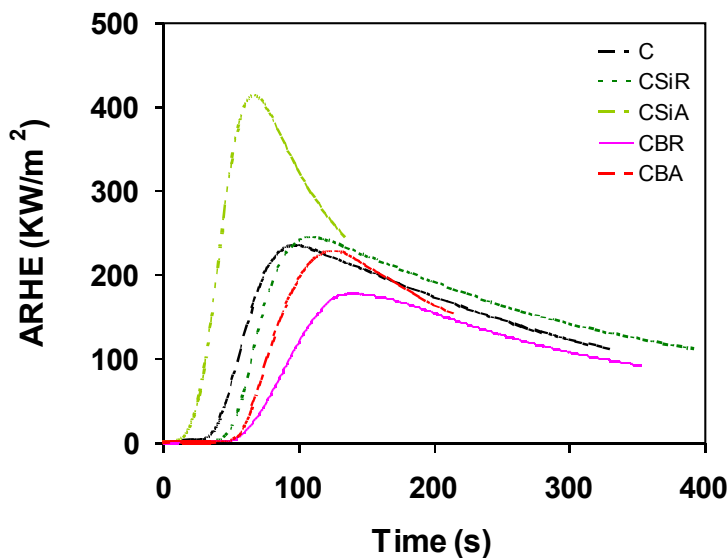


Figure 2. ARHE vs. Time for the different systems.

3.2 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] 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.

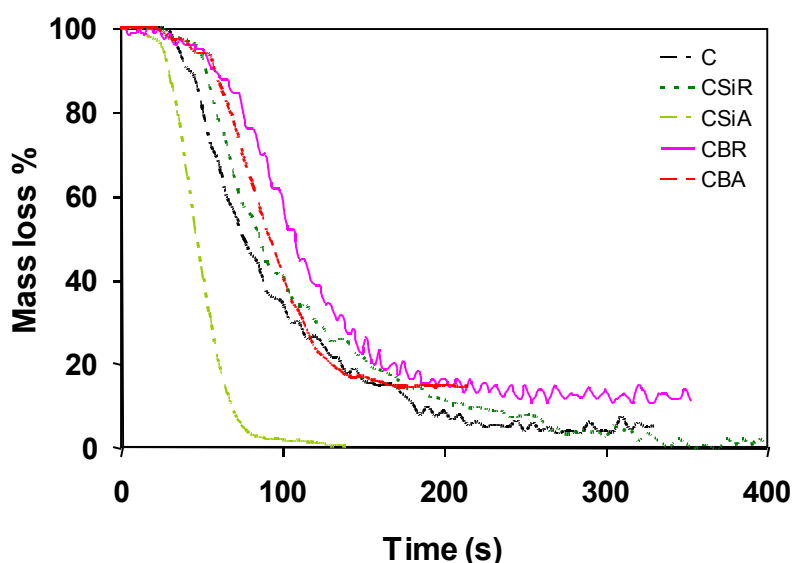


Figure 3. Mass loss curves (%) vs. Time for the different samples.

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]

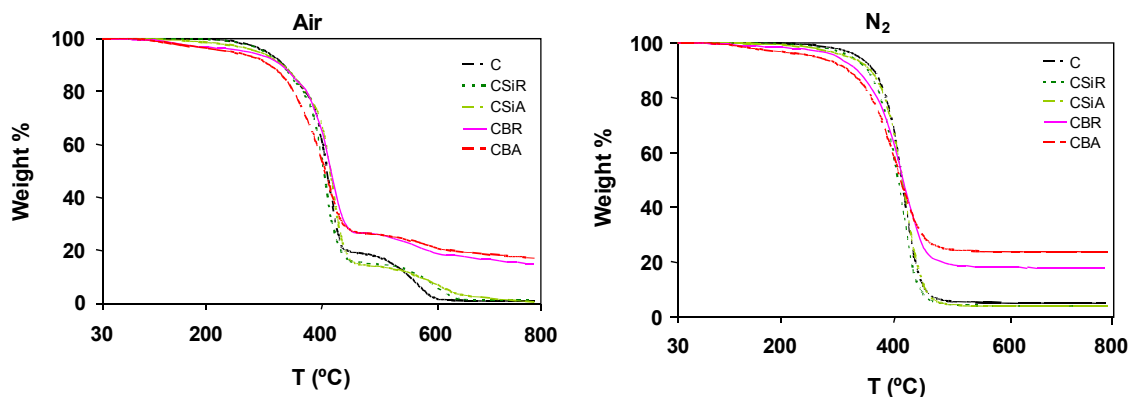


Figure 4. TGA curves of the different systems in air and N₂

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 volatilisation 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]

Table 3. Residue from cone calorimeter and termogravimetric tests.

Samples	Cone calorimeter (%)	TGA Nitrogen		TGA Air	
		T _{5%} ^a (°C)	Char ^b (%)	T _{5%} ^a (°C)	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

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 10°C/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.

3.3 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]

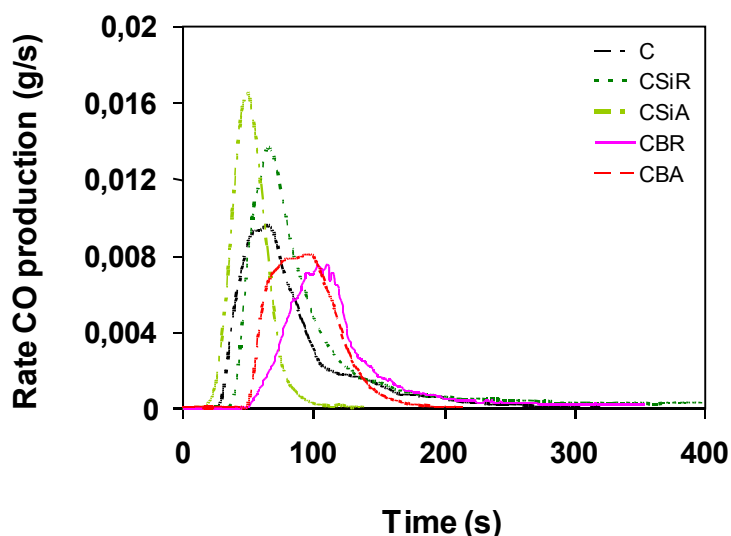


Figure 5. CO evolution vs. time for copolymers.

3.4. 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 $\text{Tan } \delta$.

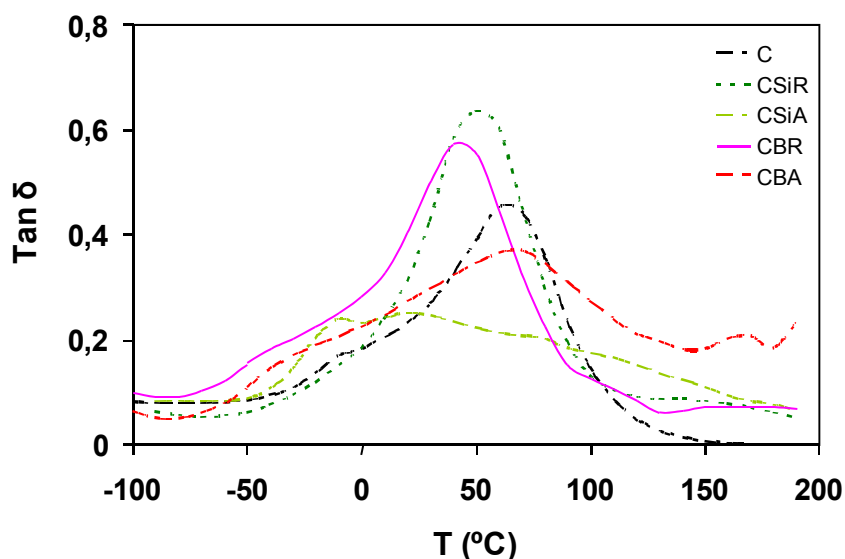


Figure 6. Tan δ of copolymers as function of temperature.

4. 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 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 and significant improvements are obtained

when reactive flame retardants are used. This may result from improved dispersion of the reactive fire retardant moieties compared to the corresponding additives, or their presence in the polymer chain may promote crosslinking and char formation.

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