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ScienceDirect
Polymer 47 (2006) 8194–8202
polymer
www.elsevier.com/locate/polymer

DSC and TGA study of the transitions involved in the thermal treatment of binary mixtures of PE and EVA copolymer with a crosslinking agent

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Received 11 July 2006; received in revised form 14 September 2006; accepted 19 September 2006
Available online 18 October 2006

Abstract

The crosslinking process of PE and EVA with different concentrations of a crosslinking agent (CA) has been studied. The extent of the crosslinking has been evaluated by gel fraction and density measurements. The different transitions involved in the thermal processing and decomposition have been studied by DSC and TGA and compared for all the mixtures prepared. Mechanistic pseudo-kinetic models have been suggested and applied involving all the fractions susceptible of undergoing transitions or reactions. The models applied can be of great interest in understanding the phenomena involved, as well as in modeling the heat effects in the whole processing or pyrolysis of this type of products.

Keywords: PE; EVA; Crosslinking

1. Introduction

The crosslinking process consists in the formation of chemical bonds (crosslinks) between adjacent molecular chains to form a three-dimensional network. Polymer crosslinking is of commercial and scientific interest due to the beneficial effect that it provides on the mechanical properties (even for long periods of time) leading to harder, stiffer, stronger and tougher products that are needed for modern applications. Crosslinked polymers are usually moulded and shaped before they are crosslinked. Once crosslinking has taken place, usually at high temperature, the object can no longer be shaped (thermoset). Not all polymers can be crosslinked, but for those that can the results may be very important.

The general effects that polymer crosslinking provides are: stability at higher temperatures and working temperatures (thermal resistance); higher tensile strength, abrasion resistance/cut through, crush resistance and over load characteristics; resistance to (environmental) stress cracking; solvent resistance (only produce a swollen gel in hydrocarbon solutions); solder iron resistance; lower free volume and higher glass transition; slightly better flame resistance; improved chemical and water treeing resistance, fluid resistance (melt viscosity) and high temperature mechanicals (even at 180 °C) such as toughness, impact resistance, long term hydrostatic strength, creep properties, resistance to slow crack growth and rapid crack propagation; no change of electricals; difficulty in recycling and decrease in flexibility and elastic properties. However, extensive crosslinking in a crystalline polymer may cause loss of crystallinity with deterioration of the mechanical properties on this fraction [1–3].

There exist several ways to produce crosslinked polymers such as chemical methods, using mainly peroxides [4] or silanes [5,6], and high-energy irradiation (electronic beam) techniques [7–9]. Thermochemical crosslinking involving organic peroxides is widely used because of its controlled decomposition rate, minimal side products and economical process [10].

Important areas of application of crosslinked polymers (especially polyethylene) are: insulation and jacketing material in power cables and wires, hot water piping installation and heat-shrinkable products. Crosslinked polymers can also be coatings, lumber, railroad tires, medical devices, tubing for industrial use (chemically inert and non-corroding, longer

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0032-3861/$ - see front matter
doi:10.1016/j.polymer.2006.09.054

Notation

a, b, c	Parameters of heat capacity
Cp	Heat capacity
$\mathrm{d}Q_\mathrm{j}/\mathrm{d}T$	Heat derivative with respect to the temperature of process j, with: $\mathrm{d}Q_\mathrm{j}/\mathrm{d}T = -\Delta H_\mathrm{j}\mathrm{d}w_\mathrm{j}/\mathrm{d}T = (-\Delta H_\mathrm{j}/\nu_\mathrm{H})(\mathrm{d}w_\mathrm{j}/\mathrm{d}t) = \Delta H_\mathrm{j}(k_{\mathrm{ref,j}}/\nu_\mathrm{H})w_\mathrm{j}^{n_i} \exp((-Ea_\mathrm{j}/R)(1/T - 1/T_\mathrm{ref}))$
DSC	Differential scanning calorimetry
$\mathrm{Ea_j}$	Activation energy of reaction j
EVA	Polyethylene vinyl acetate copolymer
$\mathrm{G_i}$	Gas produced in the thermal decomposition of specie i
ΔH_j	Constant latent heat of reaction j
$k_{\mathrm{ref,j}}$	Pre-exponential factor of reaction j at T_ref (373 K)
M	Melt state
N	Number of experimental points
n	Reaction order
O.F.	Objective function
P	Number of parameters to be fitted
PE	Polyethylene or polyethylene domains in EVA
phr	Parts per hundred of resin
R	Perfect gas constant
S	Solid state
T	Temperature
T_i	Temperature at a given time
t_i	Time (s)
TGA	Thermal gravimetric analysis
VA	Vinyl acetate domains in the EVA copolymer
V.C.	Variation coefficient
w	Mass fraction of non-transformed polymer (or non-reacted material).

Greek symbols

ν_H	Constant heating rate
ϕ_m	Weight percentage of polymer in the corresponding sample m
γ	Vinyl acetate fraction in EVA copolymer.

service life, lower maintenance costs), adhesives, electronic parts, employed in the synthesis of ion-exchange resins and stimuli-responsive hydrogels, etc. [11–14]. It is even possible to produce a superficial crosslinking in order to avoid the time migration of the different compounds of the polymer, especially in the packaging of food, pharmaceuticals or cosmetics [15–17], and to improve the compatibility of immiscible or incompatible polymers [18–20].

Finally, another usual application of the crosslinking process is to improve (or even to allow) the characteristics of foamed materials that by themselves, without a previous crosslinking, do not have many industrial applications.

The family of low-density microcellular compounds obtained by foaming and crosslinking of EVA copolymers has a large field of commercial applications where the density reduction can be turned directly into material/cost savings and more valuable products (closed-cell structure, resistant to oils and gasoline, low rates of heat transmission and small water absorption). Typical examples of such a wide range of uses of these products (flexible or rigid/resistant to compression, depending on the nature of the polymer and the type and degree of crosslinking produced) are for instance soles of sport shoes, bicycle helmets, toys, nautical buoys and parts imparting buoyancy to boats, gymnasium floors, hygienic stable floors, thermal insulation in refrigerators, portable insulated chests, cushions for furniture and automobiles, building industry (sandwich structures or hollow structural units reinforcing), etc.

Therefore, the kinetic study and accurate knowledge of the effect of the different variables (processing and product variables) on the processes involved in the thermal treatment of these crosslinking substances (transitions, melting and crosslinking) are very important [4,5,19,21–25].

In previous works [26–28], the thermal transitions and crystallinity of a commercial polyethylene (PE) and poly(ethylene-*co*-vinyl acetate) (EVA), their respective binary mixtures and the binary mixtures of PE and EVA with a foaming agent were studied by DSC. The methodology used to perform the kinetic study of the data was also introduced and discussed. Both the components and compositions of the mixtures studied are typical in commercial formulations of foamed products.

We thus considered valuable to investigate in this article the interactions among the polymeric matrix (PE or EVA) and the crosslinking agent (CA) at different concentrations, and to establish the effect of the crosslinking process on the pseudo-kinetic parameters of the thermal treatment and degradation of the PE and EVA. First of all, the thermal properties such as specific melting enthalpy, melting and degradation temperatures of uncrosslinked and crosslinked samples, and their dependence on the crosslinking agent concentration were studied by differential scanning calorimetry (DSC) and by dynamic thermal gravimetric analysis (TGA). The crosslinking degree of the samples was associated to their gel content (GC), determined by a solvent-extraction method. Also, the density evolution of the crosslinked samples was determined.

In addition, a mechanistic and pseudo-kinetic model is suggested and applied to the analysis and correlation of the DSC and TGA data. The DSC analysis presented in this paper allows for better knowledge of the crosslinking phenomena: quantification of the heat involved in the industrial processing of crosslinked products is very useful information for the optimisation of the process, cycles and formulations to be used. On the other hand, the pyrolysis of these materials, studied by TGA, has received renewed attention due to the possibility of converting their wastes into useful energetic products or into valuable chemicals.

2. Equipment and experimental procedure

2.1. Materials

The polymers used were low-density polyethylene (LDPE) PE003 and EVA PA-539 ALCUDIA® copolymer, both supplied by REPSOL YPF®. Table 1 shows the properties of these two polymers according to the supplier.

The crosslinking agent (CA) was a suitable peroxide frequently used in the production of EVA and PE foams, such as α,α'-bis(*tert*-butylperoxy)-*m*/*p*-diisopropylbenzene, TBPPB, provided by Rusimont Group-Elf Atochem® (Peroximon F-40®, Table 2). The decomposition of this peroxide occurs after the melting of the PE and EVA, i.e. in the molten polymer, favouring its crosslinking reactivity.

2.2. Sample preparation

Binary mixtures of PE or EVA with three different concentrations of TBPPB (0.75, 1.5 and 3 phr, i.e., 0.74, 1.48 and 2.91 wt%) were studied. The content of CA were selected close to typical values used in industrial applications.

The mixtures were prepared, prior to experiments, in a Brabender® Plasticorder PL 2000 extruder at 398 K with a speed of 20 rpm, using a single screw. These conditions were chosen to achieve a good homogenisation of the mixture, but avoiding the activation of the peroxide initiation reactions [29–31]. After the extrusion die, the mixture discharged was cut into pellets, immersed in a water bath and, after that, dried at room temperature.

2.3. Thermal analysis

2.3.1. Differential scanning calorimetry (DSC)

DSC tests were performed on a Perkin–Elmer® DSC 7 controlled by a PC AT compatible system. Samples of 8–9 mg were encapsulated in aluminium pans and treated at a heating rate of 10 K/min. The atmosphere used was nitrogen with a flow rate of 45 STP mL/min. To analyse the influence of the crosslinking agent before and after crosslinking, two consecutive runs to each sample were performed. Initially, the first experiment in the temperature range of 313–573 K was run. The sample was then cooled until 293 K and a second run was performed under the same heating rate, in order to analyse the effect of the crosslinking agent not only before and during the crosslinking process (first run), but also on the final crosslinked polymer (second run), i.e. to characterise the post-processing product.

Table 1
Technical data of LDPE PE003 and EVA PA-539 (ALCUDIA®, REPSOL YPF®)

Property	PE	EVA
Melt flow index (g/10 min)	2	2
Vicat temperature (°C)	92	64
Crystallinity (%)	44	18
Density at 23 °C (g/cm^3)	0.920	0.937
Melting temperature (°C)	113	90

Table 2
Technical data for Peroximon F-40® (Rusimont Group-Elf Atochem)

Properties	Value
wt% α,α'-bis(*tert*-butylperoxy)-*m*/*p*-diisopropylbenzene (TBPPB)	40
wt% inert charge ($CaCO_3$ precipitated)	60
% Active oxygen	3.78
Specific gravity (g/cm^3) at 20 °C	1.63
Density (g/cm^3)	0.71

2.3.2. Thermobalance (TGA)

The thermogravimetrical experiments were carried out using a Netzsch® Thermobalance TG209 controlled by a PC under the Windows operating system. The tests were performed in a nitrogen environment with a flow rate of 45 STP mL/min. Samples of 5 mg were heated at 10 K/min from 303 to 873 K.

In both techniques, the experiments were replicated in order to determine their reproducibility, showing very good results with a maximum deviation between the repeated runs of about 2%.

2.4. Crosslinking

To obtain the crosslinked product a hydraulic hot plates press MECAMAQ® DE-200 was used. The temperature in both plates was 448 K and with the residence time 10 min. With these conditions the crosslinking reaction was complete.

2.4.1. Density measurement

The density of the different mixtures was measured after processing using a glass picnometer at 298 K. The variation coefficient for the measured densities was estimated to be 0.005 g/cm^3.

2.4.2. Gel content measurement

The degree of crosslinking can be estimated through the gel fraction (i.e. insoluble fraction). The gel content of the crosslinked samples was determined gravimetrically (according to UNE 53-381-89) by a 16 h Soxhlet extraction cycle using decaline as solvent at 458 K in the case of the samples with PE or THF (tetrahydrofuran) at 339 K for the EVA samples. Approximately 0.3–0.4 g of the crosslinked polymer (m_0) was cut into small pieces. After the extraction cycle, the sample was dried to a constant weight (m_1) at 353 K. The gel fraction was calculated as the percentage ratio of the final weight of the polymer to its initial weight, taking also into account the initial insoluble fraction (f) of the sample. The variation obtained for repeat measurements was lower than 5%.

$$\mathrm{GC} = \left(1 - \frac{m_1}{m_0(1-f)}\right)100 \tag{1}$$

2.5. Mathematical treatment

The pseudo-kinetic parameter unknowns of the kinetic models proposed in this work have been optimised using the tool "Solver" included in the spreadsheet Excel for Windows. In all the calculations the objective function considered was:

$$\text{O.F.} = \sum_{m=1}^{4} \sum_{i=1}^{N} \left[\left(\frac{\mathrm{d}Y}{\mathrm{d}X} \right)_{\text{exp.}} - \left(\frac{\mathrm{d}Y}{\mathrm{d}X} \right)_{\text{calc.}} \right]^2 \tag{2}$$

where m represents the different samples simultaneously fitted (with different CA content), i represents the experimental data at temperature T_i and at time t_i, N is the number of experimental points, $(\mathrm{d}Y/\mathrm{d}X)_{\text{exp.}}$ represents the experimental heat or mass derivative with respect to the temperature or time, as obtained from the DSC or TGA apparatus, respectively, and $(\mathrm{d}Y/\mathrm{d}X)_{\text{cal.}}$ is the calculated value from the corresponding proposed kinetic model (Eq. (4) or (5)).

In order to compare different kinetic models a variation coefficient is introduced:

$$\text{V.C.}(\%) = \left| \frac{\sqrt{\text{O.F.}/N - P}}{D_{\text{exp.av.}}} \right| 100 \tag{3}$$

where P is the number of parameters to be fitted and $D_{\text{exp.av.}}$ is the average of the experimental derivatives. The integration of the kinetic equations was carried out using the Euler method.

3. Results and discussion

In this section, the PE and EVA crosslinking process through chemical reactions with a different amount of TBPPB peroxide used as crosslinking agent is discussed.

3.1. Physical properties of the crosslinked samples

The results of density and gel content for the crosslinked samples are shown in Fig. 1 to confirm the effect of the crosslinking reaction. The densities of the pure polymers (PE and EVA) without crosslinking are also given as a reference in comparison with the samples crosslinked with different amounts of peroxide. As expected, the presence and increase in CA concentration produces an increase in the final density and gel content of the sample as a consequence of a larger crosslinking degree of the new structure generated.

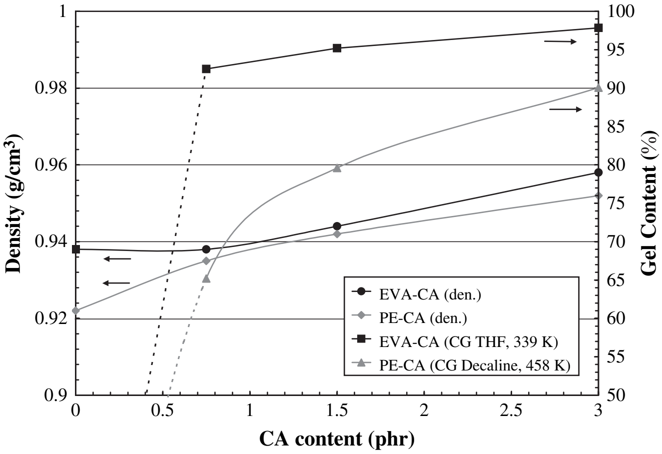

Fig. 1. Density and gel content (indicating solvent and temperatures used) of the samples studied. Pressed samples at 175 °C during 10 min.

3.2. Thermal properties and analysis

3.2.1. DSC experiments

Tables 3 and 4 show the melting temperatures (or reaction temperature in the case of the crosslinking agent) and heat (i.e. area under the corresponding peak), determined by DSC measurements, for all the samples studied including pure components, uncrosslinked samples (first DSC run) and crosslinked samples (second DSC run).

For PE samples, the degree of crystallinity was calculated via the total enthalpy method according to the equation $X_C\ (\%) = \Delta H_m / \Delta H_m^+$, where X_C is the degree of crystallinity, ΔH_m is the specific enthalpy of melting of the sample studied and ΔH_m^+ is the specific enthalpy of melting for 100% crystalline PE (288 kJ/kg) [1,32].

3.2.1.1. DSC for first runs. Analysing the first run for the PE–CA and EVA–CA binary mixtures studied (Tables 3 and 4), the peaks corresponding to the thermal transitions of the polymeric matrix are similar (number of peaks, reaction temperatures and heat) to those corresponding to the pure polymers used [26], taking into account that the decomposition of the crosslinked agent (TBPPB) only presents an exothermic peak corresponding to the decomposition of this peroxide from 400 to 490 K, and therefore, after the thermal transitions of both polymers.

However, the temperature observed in the peak corresponding to the thermal decomposition of the CA, in both type of mixtures (PE–CA and EVA–CA), increase gradually when increasing the content of the CA. As can be seen in Fig. 2, the presence of the crosslinked agent also produces a relative increase of the initial (at low temperatures) and final (at high temperatures) base lines that means an increase of the apparent heat capacities of the sample. Obviously, the peak area (J/sample g) corresponding to the thermal decomposition of the crosslinking agent increases with the concentration of this agent in the mixture, but this increase does not mean any variation of its specific decomposition enthalpy (J/CA g) as will be shown in the quantitative kinetic analysis.

3.2.1.2. DSC for second consecutive runs. DSC curves for the second consecutive run of PE–CA mixtures, presented in Fig. 3, show a progressive decrease in the peak temperature

Table 3
DSC results (1st and 2nd runs) of PE, CA (TBPPB) and binary PE–CA mixtures: 0.75, 1.5 and 3 phr of CA

DSC run	Sample code	Crystallinity degree (%)	$\Delta H_{\text{melt.PE}}$ (J/g)	$T_{\text{melt.PE}}$ (K)	$\Delta H_{\text{decomp.CA}}$ (J/g)	$T_{\text{decomp.CA}}$ (K)
1st	PE	28.23	81.3	387.8	–	–
2nd		*27.67*	*79.7*	*387.8*	–	–
1st	TBPPB	–	–	–	−432.2	458.6
1st	P-T(0.75)	27.74	79.9	387.3	−1.90	468.3
2nd		*24.97*	*71.9*	*385.5*	–	–
1st	P-T(1.5)	27.88	80.3	388.0	−4.00	469.5
2nd		*23.72*	*68.3*	*383.8*	–	–
1st	P-T(3)	27.78	80.0	387.8	−8.30	471.0
2nd		*22.26*	*64.1*	*381.8*	–	–

Table 4
DSC results (1st and 2nd runs) of pure EVA and binary EVA–CA mixtures: 0.75, 1.5 and 3 phr of CA (TBPPB)

DSC run	Sample code	$\Delta H_{\mathrm{melt.EVA}}$ (J/g)	$T_{\mathrm{trans\ EVA}}$ (K)	$T_{\mathrm{melt.EVA}}$ (K)	$\Delta H_{\mathrm{melt.PE}}$ (J/g)	$T_{\mathrm{melt.PE}}$ (K)	$\Delta H_{\mathrm{decomp.CA}}$ (J/g)	$T_{\mathrm{decomp.CA}}$ (K)
1st	EVA	57.3	320.7	343.8	0.8	386.1	–	–
2nd		*52.7*	*320.1*	*343.8*	*0.8*	*386.1*	–	–
1st	E-T(0.75)	56.0	322.2	345.6	0.7	386.3	−2.8	464.5
2nd		*40.7*	*322.5*	*342.5*	*0.6*	*382.8*	–	–
1st	E-T(1.5)	58.6	320.5	345.0	0.8	386.2	−8.7	468.5
2nd		*36.9*	*321.0*	*340.5*	*0.7*	*381.0*	–	–
1st	E-T(3)	58.2	322.5	345.3	0.8	385.3	−15.6	470.3
2nd		*30.3*	*322.0*	*338.8*	*0.6*	*378.5*	–	–

and enthalpy for the PE melting process of the samples studied when increasing the content of CA, as a consequence of the increase of the corresponding crosslinking degree, previously commented in the gel content study. Therefore, the samples present less crystallinity after the crosslinked reaction carried out in the DSC capsule. There also exists a larger and progressive increase of the initial and final base line slopes when the concentration of the CA in the sample is increased, showing the effect of the crosslinking process increasing the apparent heat capacities.

If the second consecutive heating run of the EVA mixtures is considered (Fig. 3 and Table 4), the first peak for EVA contribution appears at progressively lower temperatures when increasing the CA content, and undergoing a noticeable (and progressive) decrease in its height and total area, in the same way as happens in pure EVA [26]. The second and third peak also undergoes a continuous decrease in the peak temperature and area, compared with the first run, when the crosslinking agent is increased. Furthermore, the third peak corresponding to the melting of the ethylene domains of the EVA copolymer presents a sensitive lesser variation than the previous peaks (corresponding to the vinyl acetate domains).

The progressive decrease in the temperatures and heat of the different transitions, and therefore in the degree of crystallinity of the crosslinked samples observed, when increasing the CA content (that is, increasing the crosslink density), is due to the reduction in the structural regularity that the created crosslinks introduce, impeding or disturbing the reorganization and also the folding of macromolecular chains, decreasing in general the size and content of the crystals [4,5,33].

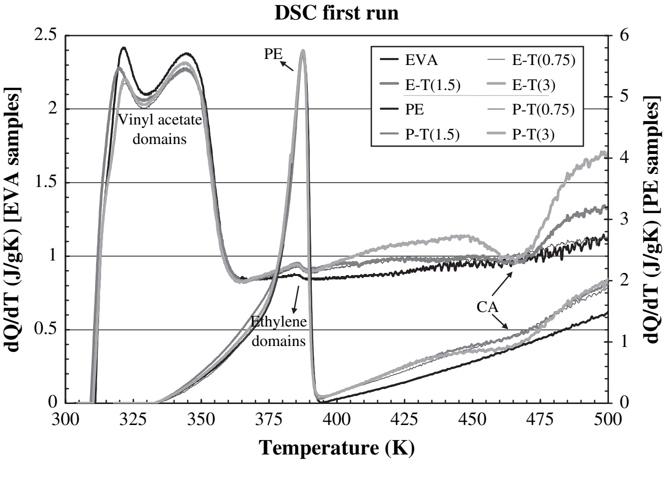

Fig. 2. DSC results (1st runs) for the pure polymers and binary mixtures: 0.75, 1.5 and 3 phr of CA (TBPPB).

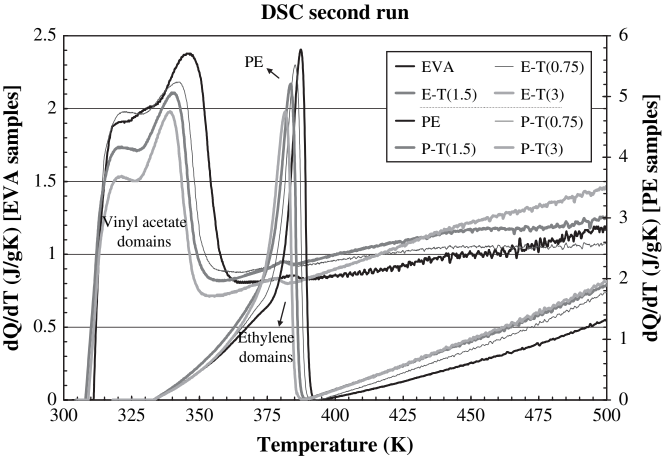

Fig. 3. DSC results (2nd runs) for the pure polymers and binary mixtures: 0.75, 1.5 and 3 phr of CA (TBPPB).

The base lines after the polymer peaks, for both runs of each sample, are very similar. Therefore, the base line slope should depend mainly on the crosslinking process, certifying the new structure formed. Finally, it can also be observed that for all the second run experiments no more CA decomposition peaks appear, indicating that TBPPB was consumed completely during the first runs.

In the case of the EVA samples, the acetate groups of the EVA copolymer help the formation of radicals in a larger extent than in the case of the PE [34–38], therefore, as can be deduced previously, the EVA copolymer undergoes a larger modification as a consequence of the crosslinking process than the PE polymer.

3.2.2. TGA experiments

The general shape of the thermal degradation of the polymeric matrix (PE or EVA) of the binary samples studied is similar to that corresponding to pure polymer, presenting 1 or 2 steps, respectively [26]. However, there is a progressive shift in all decomposition processes to higher temperatures when increasing the peroxide content, in both PE–CA and EVA–CA binary samples.

As an example, Fig. 4 shows the TGA curves for the commercial CA and EVA–CA binary samples (peak temperatures for all the mixtures studied are shown in Table 5). As expected, the CA presents a thermal degradation with only one-step, around 460 K, and a final solid residue corresponding to 60% of the initial weight. The EVA–CA samples show a first peak corresponding to the VA loss and a second peak (equivalent to the PE samples) corresponding to the decomposition of the polyolefin chain resulting from the first process and of the PE domains of the polymer. A magnification of the range of temperatures where the CA undergoes decomposition is presented, clearly showing that this process is visually proportional to the amount of CA used.

3.3. Kinetic models

The pseudo-kinetic study of the process would be a very important aspect to quantify and simulate the evolution of the different species present in the sample compounds (with the temperature or time), also to determine the amount of gases evolved and may help in the optimisation of industrial processing.

It is widely accepted that crosslinking reactions go through free radical mechanisms. In general, the free radicals generated on thermal decomposition of peroxides can attack the molten polymer chains (abstracted the hydrogen atoms to produce alkyl radicals) and the crosslinking of the polymer chains may occur. Examples of radical reaction mechanism of crosslinking are proposed in literature [33,39,40].

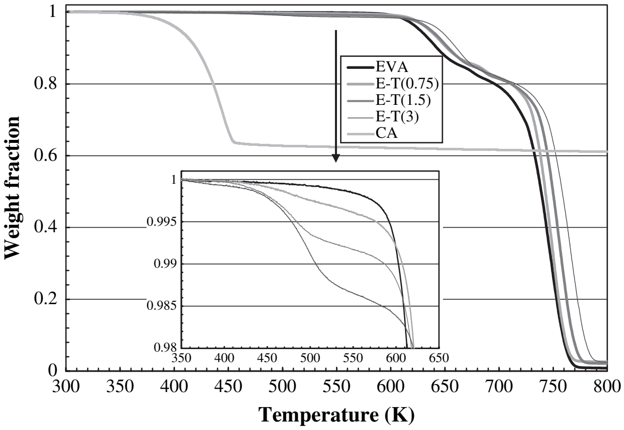

Fig. 4. Experimental TGA curves for the CA (TBPPB), pure EVA and EVA–CA mixtures studied with 0.75, 1.5 and 3 phr of CA.

Table 5
TGA peak temperatures (K) of the samples studied

	$T_{\text{peak PE}}$	$T_{\text{peak CA}}$		$T_{\text{peak1 EVA}}$	$T_{\text{peak2 EVA}}$	$T_{\text{peak CA}}$
TBPPB	–	445				
PE	747	–	EVA	639	747	–
P-T(0.75)	749	485	E-T(0.75)	649	754	490
P-T(1.5)	754	485	E-T(1.5)	655	759	490
P-T(3)	760	485	E-T(3)	662	769	490

But the aim of the present study is to evaluate the effects that the crosslinking process produces on the global pseudo-kinetic constants of the different thermal transitions and degradation of the systems studied. Therefore, the following pseudo-kinetic models, which start from a linear combination of the effects that the different components cause considering the concentration of each compound in the different PE–CA and EVA–CA binary mixtures, have been suggested and applied involving all the fractions susceptible of undergoing thermal reactions in DSC and TGA experiments, respectively:

$$\frac{\mathrm{d}Q^{\mathrm{DSC}}_{\mathrm{Polymer-CA}(m)}}{\mathrm{d}T} = w_{\mathrm{S}}\mathrm{Cp}_{\mathrm{S}} + \frac{\mathrm{d}Q^{\mathrm{DSC}}_{\mathrm{Polymer}}}{\mathrm{d}T}\phi_m + \frac{\mathrm{d}Q^{\mathrm{DSC}}_{\mathrm{CA}}}{\mathrm{d}T}(1-\phi_m) + (1-w_{\mathrm{S}})\mathrm{Cp}_{\mathrm{M}} \tag{4}$$

$$\frac{\mathrm{d}w^{\mathrm{TGA}}_{\mathrm{Polymer-CA}(m)}}{\mathrm{d}t} = \frac{\mathrm{d}w^{\mathrm{TGA}}_{\mathrm{Polymer}}}{\mathrm{d}t}\phi_m + \frac{\mathrm{d}w^{\mathrm{TGA}}_{\mathrm{CA}}}{\mathrm{d}t}(1-\phi_m) \tag{5}$$

In order to obtain better correlation to fit all the experimental data of the whole DSC curve, due to the existence of a strong base line variation, the contribution of the apparent heat capacities (Cp) of the solid (w_{S}) and melted ($1-w_{\mathrm{S}}$) fractions with the temperature have also been included in the model.

In previous papers, Marcilla et al. suggested and applied a pseudo-kinetic model and a methodology to model and explain the thermal transitions and fusions involved in the thermal treatment of polymers (such as PE and EVA) prior to their decomposition [26,27], and the thermal (and catalytic) pyrolysis of PE and EVA polymers [41,42]. These previous models use *n*-order kinetics and Arrhenius type behaviour of the rate constant, and can be developed and applied in an equivalent way for our analysis to model the different individual contributions in the binary samples studied, following the corresponding scheme of reactions (Table 6). The average of the variation coefficients obtained are 0.23 for the DSC curves (1200 points) and 0.51 for the TGA experiments (1679 points).

The total number of parameters that have to be fitted depends on the polymeric matrix studied (number of peaks). Thus, in the DSC experiments, using 4 parameters for single reaction peak (ΔH, k_{ref}, Ea and n), for one PE–CA sample the model presents 14 parameters to be optimised (2 reactions + 2 line base correction) and for an EVA–CA mixture the model has 23 parameters (4 reactions + 2 line base correction + 1 unknown fraction). In the case of the TGA, the total number of parameters to be optimised is 7 for

Table 6
General scheme of reactions of the materials studied (CA, EVA and PE) in DSC and TGA experiments

DSC	TGA
$\mathrm{CA} \xrightarrow{k_{\mathrm{D,CA}}} s_{\mathrm{CA}}R_{\mathrm{CA}} + (1-s_{\mathrm{CA}})\mathrm{G}_{\mathrm{CA}}$	$\mathrm{CA} \xrightarrow{k_{\mathrm{D,CA}}} s_{\mathrm{CA}}R_{\mathrm{CA}} + (1-s_{\mathrm{CA}})\mathrm{G}_{\mathrm{CA}}$
$\mathrm{EVA} \xrightarrow{k_{\mathrm{T,EVA}}} \mathrm{EVA(T)} \xrightarrow{k_{\mathrm{M,EVA}}} \mathrm{EVA(M)}$	$\mathrm{EVA} \xrightarrow{k_{\mathrm{D1,EVA}}} s_{\mathrm{EVA}}\mathrm{EVA}^{*} + (1-s_{\mathrm{EVA}})\mathrm{G}_{\mathrm{EVA}}$
$\mathrm{PE} \xrightarrow{k_{\mathrm{M,PE}}} \mathrm{PE(M)}$	$\mathrm{EVA}^{*} \xrightarrow{k_{\mathrm{D2,EVA}}} \mathrm{G}_{\mathrm{EVA}^{*}}$
$\mathrm{PE} \xrightarrow{k_{\mathrm{M,PE}}} \mathrm{PE(M)}$	$\mathrm{PE} \xrightarrow{k_{\mathrm{D,PE}}} \mathrm{G}_{\mathrm{PE}}$

a PE–CA sample ($2 \times k_D$, $2 \times (\mathrm{Ea}/R)$, $2 \times n$, s_{CA}) and 11 for an EVA–CA binary mixture ($3 \times k_D$, $3 \times (\mathrm{Ea}/R)$, $3 \times n$, and the coefficients s_{EVA} and s_{CA}). This number of parameters may appear too high but the number of the separate processes/peaks analysed must be considered, taking into account the evolution of the apparent heat capacities and that any linearization has been made.

In the case of the correlation of the second DSC run, where the samples are already crosslinked and no more CA is present in the sample, the corresponding CA term in Eq. (4) is removed.

3.3.1. DSC kinetic model analysis

In the simultaneous correlation of the first DSC run for the PE–CA and EVA–CA samples, all the pseudo-kinetic parameters are constant (validating the linear combination of the individual behaviour of the components) except that corresponding to the Cp contributions (for solid and melted species) that necessarily have been fitted independently for each binary sample, indicating the influence of the crosslinking agent and sample crosslinking degree in the internal heat transfer. Fig. 5a,b shows an example of the deconvolution of the calculated curves and the satisfactory degree of the correlation obtained. In these figures, we can also observe the contribution of the different components and reactions to the global DSC curve.

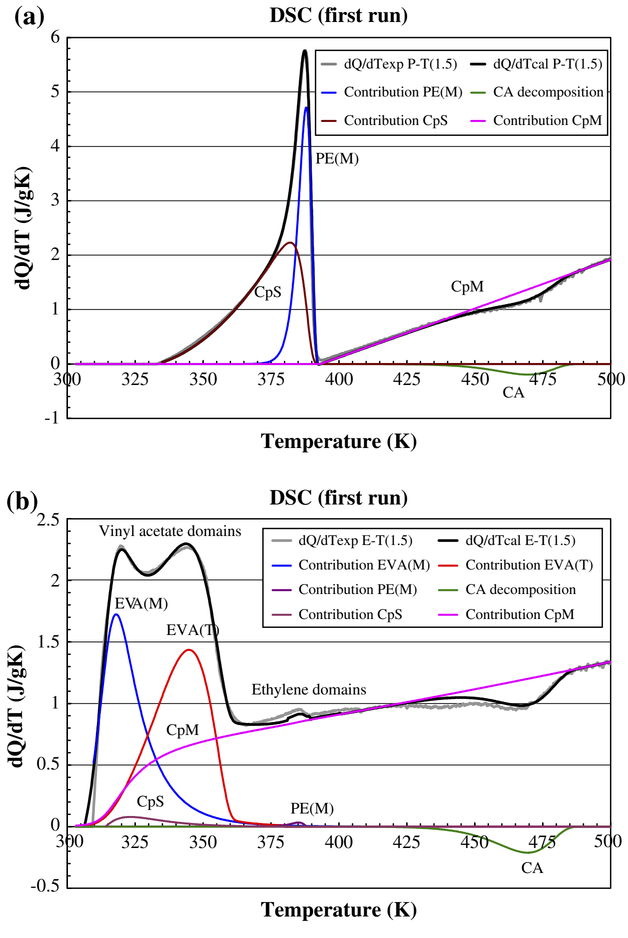

Fig. 5. Experimental and calculated DSC curves (first run) with the different contribution of each component for the mixtures (a) PE–CA and (b) EVA–CA, both with 1.5 phr of CA (TBPPB).

The evolution of the Cp contribution in the different PE–CA and EVA–CA samples (with different CA content) is the following: the contribution of $\mathrm{Cp_M}$ and $\mathrm{Cp_S}$ increase when increasing the CA content, especially at larger temperatures. In the case of EVA DSC curves, the contribution of $\mathrm{Cp_S}$ is less than in the case of PE, as can be seen by the absence of important slope variations before the corresponding EVA peaks.

In the case of the second DSC run, i.e. once the polymeric matrix is already crosslinked, there exists a change in the location and area of the peaks associated to the melting processes of the corresponding polymers. This feature shows that the linear combinations no longer apply and thus it is necessity to allow the variation of the corresponding pseudo-kinetic parameters with the crosslinking agent concentration (apart from those corresponding to the Cp contributions), in order to obtain a satisfactory fit.

In the case of the PE–CA samples, the parameters that have been fitted independently for each curve (binary sample) are: $\Delta H_{\mathrm{M.PE}}$ and $k'_{\mathrm{ref,M,PE}}$ while in the case of the crosslinked EVA samples: $\Delta H_{\mathrm{T,EVA}}$, $\Delta H_{\mathrm{M.EVA}}$, $\Delta H_{\mathrm{M.PE}}$, $k'_{\mathrm{ref,T,EVA}}$ (but only for the pure EVA), $k'_{\mathrm{ref,M,EVA}}$, $k'_{\mathrm{ref,M,PE}}$, $\mathrm{Ea_{M,EVA}}$ and $n_{\mathrm{M,EVA}}$. Fig. 6 shows as an example, the excellent results obtained for the binary samples PE–CA and EVA–CA, both with 1.5 phr of CA.

In short, the variation (with the CA content) of the different pseudo-kinetic parameters fitted independently for each sample are the followings: for the crosslinked PE, $\Delta H_{\mathrm{M.PE}}$ and $\log(k'_{\mathrm{ref,M,PE}})$ present an approximate linear behaviour; and for the crosslinked EVA samples, $\Delta H_{\mathrm{M.PE}}$, $\mathrm{Ea_{M,EVA}}$, $n_{\mathrm{F,EVA}}$ and $\log(k'_{\mathrm{ref,F,EVA}})$ present an approximate linear behaviour while $\Delta H_{\mathrm{T,EVA}}$, $\Delta H_{\mathrm{M.EVA}}$ and $\log(k'_{\mathrm{ref,M,PE}})$ have a parabolic one.

On the other hand, in the crosslinked PE, the contribution of $\mathrm{Cp_S}$ decreases with the sample crystallinity when increasing the CA, while the $\mathrm{Cp_M}$ contribution increases. In the case of the crosslinked EVA, both $\mathrm{Cp_S}$ and $\mathrm{Cp_M}$ increase with the crosslinking degree.

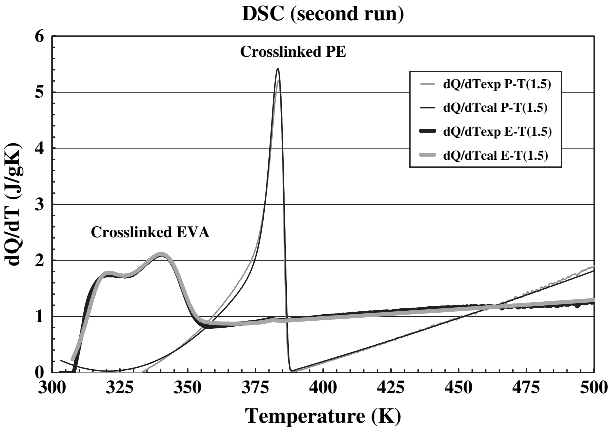

Fig. 6. Experimental and calculated DSC curves (second run) for the mixtures PE–CA and EVA–CA with 1.5 phr of CA (TBPPB).

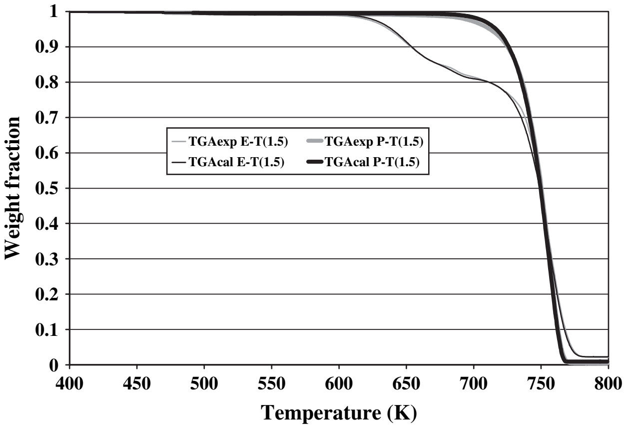

Fig. 7. Experimental and calculated TGA curves for the mixtures (a) PE−CA and (b) EVA−CA, both with 1.5 phr of CA (TBPPB).

The increase of the apparent heat capacity shows the effect of the new structure (with greater viscosity and molecular weight) generated by the crosslinking reaction, decreasing the thermal conductivity inside the sample.

3.3.2. TGA kinetic model analysis

As commented before, a progressive displacement in the decomposition temperatures to higher values can be observed, in both series of PE and EVA crosslinked samples, when increasing the crosslinking degree. Obviously this variation causes the variation of the corresponding pseudo-kinetic parameter with the concentration of the CA, as in the correlation of the second DSC run, since in TGA the decomposition of the polymer is studied and this happens after the CA decomposition, so the sample is therefore already crosslinked. In this case, we have considered this effect in the pre-exponential factors that are directly related with the temperature of maximum degradation, while the Ea and *n* have been kept constant for each series of samples. Therefore, these pre-exponential factors for all the related reactions have to be independently optimised for each sample (with different concentration of CA), in order to obtain a simultaneous and satisfactory fit of the crosslinked samples. It is necessary to observe that all the pseudo-kinetic parameters corresponding to the pure polymers (PE or EVA) have also been optimised independently, due to the effect of the crosslinking process introduced in the initial polymeric matrix. In this case, the logarithm of the pre-exponential factors corresponding to the thermal degradation of the PE (1 step) and EVA (2 step) presents an almost linear tendency with the CA content of the crosslinked samples.

As an example, Fig. 7 presents the experimental and calculated TGA curves for the binary samples with 1.5 phr of CA showing an excellent degree of coincidence.

4. Conclusions

Investigation of the thermal properties of the uncrosslinked binary samples showed that the melting point, heat of fusion and crystallinity of the pure polymer are not significantly modified by the presence of the peroxide before the crosslinking process (DSC first run). In the crosslinked samples (second DSC run), the increase of the crosslinking degree also produces a decrease of the melting point, heat of fusion and crystallinity, and on the other hand, an increase of the density and the thermal decomposition temperature (TGA). Therefore, crosslinking produces a delay or a stability effect on the main decomposition process of the PE and EVA studied.

The models proposed satisfactorily fit the different calorific processes that occur in the different uncrosslinked and crosslinked materials studied by the DSC and TGA technique, even when complex and overlapped peaks are present. These models specially include the evolution of the apparent heat capacities, the decrease of the melting point, heat of fusion and crystallinity in the crosslinked samples (second DSC run), and the increase of the thermal decomposition temperature (TGA). These results can be used to control the thermochemical crosslinking process (including the heat capacity contribution), to optimise the energy requirements and the properties of crosslinked polymers, and to simulate the thermal degradation of crosslinked samples.

Acknowledgements

Support for this work was provided by "Generalitat Valenciana", Research projects: GRUPOS03/159, GV01-42 and GR01-36.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2006.09.054

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