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Synergetic effect of poly(vinyl butyral) and calcium carbonate on thermal stability of poly(vinyl chloride) nanocomposites investigated by TG–FTIR–MS

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Abstract In order to improve poly(vinyl chloride) (PVC) thermal stability, poly(vinyl butyral) (PVB) matrix and calcium carbonate nanoparticles were incorporated in plasticized PVC. Thermal properties of these composites were investigated by thermogravimetry analysis coupled with mass spectrometry and Fourier transform infrared spectroscopy (FTIR). This approach highlighted the efficiency of both PVB and $CaCO_3$ as HCl scavengers by postponing both the onset degradation temperature and the HCl release. Moreover, a synergetic effect was evidenced regarding the HCl release. Finally, kinetic parameters of the PVC first degradation stage, determined using the Flynn–Wall–Ozawa's method, revealed a significant increase of the activation energy by incorporation of $CaCO_3$ in the presence or not of PVB.

Keywords Plasticized poly(vinyl chloride) · Nanocomposites · Poly(vinyl butyral) · Calcium carbonate · Thermal stability

Introduction

Polyvinyl chloride (PVC) has been widely used as an important commodity plastic for many years due to its non-flammability, excellent corrosion resistance, electrical insulating properties, abrasion resistance, and low cost. However, the main drawbacks of PVC are related to its low thermal stability during its processing and use, release of chlorhydric acid being dramatic for many applications.

Under nitrogen, PVC thermal degradation occurs in two major mass loss steps [1–4]. The first stage of the process consists in a dehydrochlorination sequential reaction (Scheme 1), including initiation, propagation, and termination steps. Initiation of the reaction comes from structural defects of PVC backbone, such as tertiary chlorides and allylic chlorides formed during polymerization and results in HCl release and formation of double bonds. During propagation step, these groups elongate into allylic chain very rapidly into polyene sequences. Both initiation and propagation steps involve either ion pairs or quasi-ionic concerted mechanism (Scheme 1). Termination step mechanism still has to be clearly identified. However, it is supposed to involve reactions such as intermolecular or intramolecular Diels–Alder cyclizations of the polyene sequences yielding to aromatic compounds (Scheme 2). An important aspect in the thermal degradation of the PVC is the autocatalysis of the dehydrochlorination step, which certainly occurs via a radical-cation mechanism [5]. According to Starnes et al. work, when the concentration of HCl and polyenes have reached a certain level, these products react to form polyenyl cation radicals that leads to autocatalysis. More precisely, protonation of polymer and/or polyene sequences, formed after HCl release via ionic or quasi-ionic mechanism followed by thermal excitation, yields to cation diradicals and/or monoradicals as shown in Scheme 1. The presence of these radicals was also evidenced by Han and Elsenbaumer [6]. Since these cation radicals are able to abstract an hydrogen atom from the polymer, they play an essential role in the autocatalysis process of this first degradation step.

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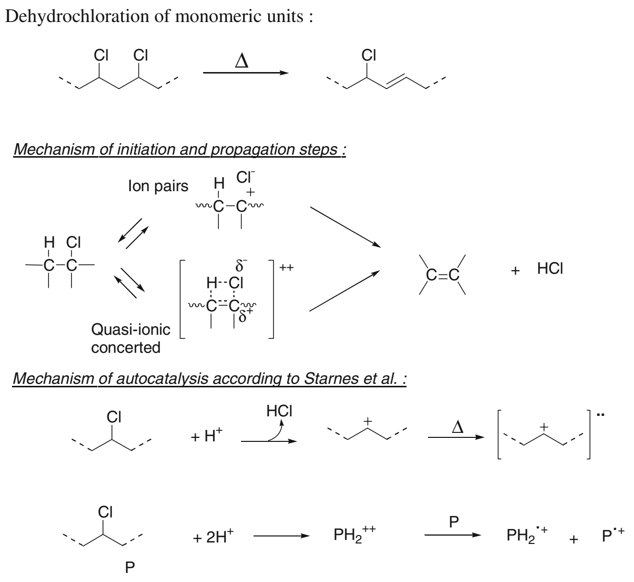
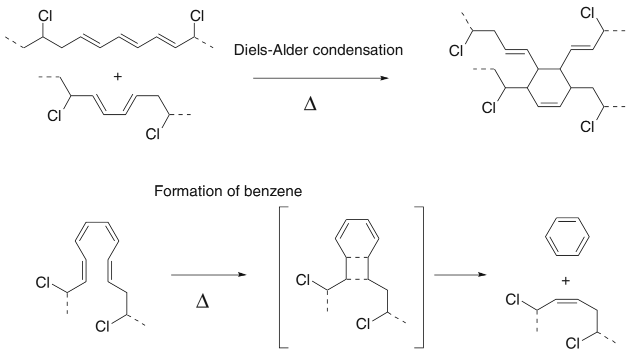


Scheme 1 Mechanism of PVC thermal degradation



Scheme 2 Cross-linking reactions during PVC thermal degradation

In order to improve PVC thermal stability, many efforts have been made to eliminate structural defects created during polymerization process. However, even if elimination of these irregularities, by changing the polymerization process or by special treatments of the polymer matrix, can improve PVC thermal stability, degradation occurs at low temperature from normal monomers, and specific stabilizers must be used. Two approaches can be considered to enhance PVC thermal stability: by adding barrier properties [7, 8] and by HCl trapping. Additives such as metallic carboxylates [9–11], basic compounds [12], organotin compounds [13], epoxy compounds [14], and fully organic compounds [15–17] are commonly used.

These stabilizers can act according two ways:

- by reacting with labile chlorine atoms in PVC chain, such as allylic or tertiary chlorines, preventing further dehydrochlorination. This process should be faster than the chain propagation itself and thus requires a very active nucleophile. As these stabilizers prevent the formation of conjugated double bonds in the polymer matrix, they are called primary stabilizers,
- by scavenging the hydrogen chloride formed during degradation of the polymer. By scavenging HCl, this kind of stabilizers avoids the autocatalytic degradation. Because they cannot prevent the deshydrochorination in its early stages, they are referred as secondary stabilizers.

However, some of them are toxic and cause environmental problems, as most of them leave toxic residues during their degradation. More recently, several alternatives, like binary blends containing poly(vinyl butyral), poly(acrylonitrile butadiene styrene), poly(methyl methacrylate butadiene styrene), poly(methyl methacrylate) [18, 19], copolymers of poly(vinyl chloride-co-vinyl acetate) [20], or incorporation of nanocharges such as layered silicates or calcium carbonate [21–23], have been studied especially to limit or delay the dehydrochlorination process for their different stabilizing modes. In this study, effect of poly(vinyl butyral) and calcium carbonate and their combination on plasticized PVC thermal degradation have been investigated using thermogravimetry. Miscibility of PVC and PVB has been reported in the literature. Mohamed et al. [18] have found that non-plasticized PVC and PVB, prepared by mixing in THF, were miscible since the glass transition temperature of the blends were in correlation with the Fox equation. However, this result has been controversial by Peng and Sui [24] in which they found only a fully miscibility up to 10% PVB content in PVC, and for higher content only a partial miscibility in the case of blends prepared by the phase inversion method. These contradictory results can provide from different used raw materials (polymers differing by their molecular weights, their polymerization production, tacticity), and blending methodology. In the present study, all the materials have been prepared by melt compounding using process additives relative to PVC matrix. Due to the presence of DEHP as plasticizer, T_g values of the PVC/PVB blends, obtained from DSC analysis (not shown here), were too near to determine the presence of one or two glass transitions and thus to evaluate the miscibility degree of the constituents. Regarding the thermal properties, not only a stabilizing effect and chorine scavenger property have been evidenced for both PVB and $CaCO_3$, but a synergetic stabilizing effect has also been highlighted by delaying both the degradation temperature and much more significantly the hydrogen chloride release. Thermal degradation of all studied materials has been investigated using thermogravimetry–mass spectrometry–Fourier transform infrared (TG–MS–FTIR) coupling technology that constitutes a powerful tool for studying the composite thermal stability and by determining the volatile species evolved during material degradation [25–27]. As HCl plays a catalytic role in PVC thermal degradation, it has been important to follow its ion fragment by mass spectrometry during thermal measurement to evidence the efficiency of employed additives. Moreover, this technique is effective in identifying the stabilization mechanism of used additives. Finally, in order to determine kinetic parameters of the first degradation step, Flynn–Wall–Ozawa's model was applied.

Experimental

Raw materials

Both poly(vinyl chloride) (PVC) and poly(vinyl butyral) (PVB) used in this study were purchased from Scientific Polymer Products, Inc. Their molecular masses were about 120,000 and 180,000 g mol^{-1}, respectively.

PVB is commercially prepared by an acid-catalyzed butyraldehyde condensation with poly(vinyl alcohol) (PVA). Since this reaction does not proceed to complete conversion to PVB and since PVA is obtained by hydrolysis of poly(vinyl acetate) (PVAc), commercial PVB contains a certain proportion of these three polymers and corresponds exactly to the ter-polymer poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), with 11% of poly(vinyl alcohol) and 1% of poly(vinyl acetate) (Fig. 1).

Process additives, di(2-ethylhexyl) phthalate (DEHP) and zinc stearate (Zn(St)$_2$), were provided by Scientific Polymer Products. Calcium carbonate nanoparticles (Socal 312V) were supplied by Solvay. All materials were used as received.

Sample preparation

All samples were obtained by compounding PVC and PVB powders, processing additives (30 phr of DEHP and 5 phr of Zn stearate) and/or CaCO$_3$ nanoparticles (3, 5, 8, and 10 phr) in a twin-screw extruder (DSM Xplore 15 Microcompounder). All of these compounds were melted at 170 °C for 5 min at 200 rpm (rotor speed) under argon.

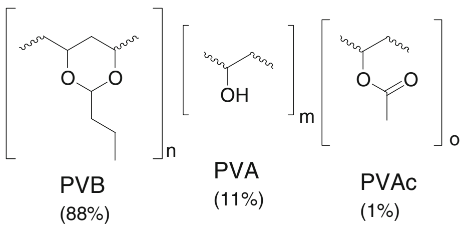


Fig. 1 Chemical structure of commercial PVB

Characterization

Morphology of nanocomposites was analyzed by transmission electron microscopy (TEM). TEM observations were performed with a Phillips CM100 equipment using an acceleration voltage of 100 kV. Ultrathin sections of composites (ca. 80 nm thick) were prepared at −130 °C with a Reichert-Jung Ultracut 3E, FC4E ultra-cryomicrotome equipped with a diamond knife.

Thermogravimetric analyses (TG) were performed under nitrogen flow (100 mL min^{-1}) at a heating rate of 10 K min^{-1} from 30 to 700 °C with a STA 409 PC from NETZSCH. The measurements were repeated three times for each sample to confirm the results. The thermogravimetric measurements were coupled with a quadrupole mass spectrometer (MS) Aëolos 403C from NETZSCH and a Fourier transform infrared spectrophotometer (FTIR) TENSOR 27 from BRUKER to identify the species evolved from the sample during the thermogravimetric experiments. Thermogravimetric measurements have also been performed at several heating rate (5, 10, 15 and 20 K min^{-1}) for degradation kinetic investigation.

Results and discussion

Nanocomposites morphology

TEM micrographs (Figs. 2, 3) of PVC nanocomposites exhibit a good dispersion of CaCO$_3$ nanoparticles. However, despite the stearic acid as surface modifier of the particles, numerous agglomerates were observed. In Fig. 3,

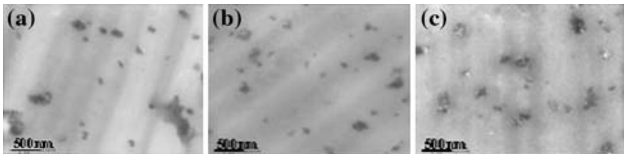


Fig. 2 TEM micrographs for plasticized PVC/CaCO$_3$ composites containing 3 phr (**a**), 5 phr (**b**), and 8 phr (**c**) of nanofillers

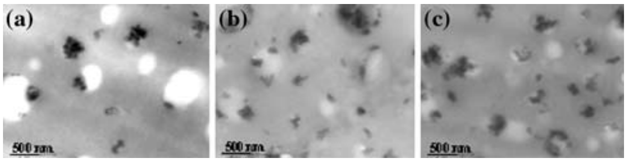


Fig. 3 TEM micrographs for plasticized PVC/PVB/CaCO$_3$ composites containing 10 phr of PVB and 3 phr (**a**), 5 phr (**b**), and 8 phr (**c**) of nanofillers

white areas correspond to PVB matrix around which nanofillers tend to aggregate due to interactions between stearic acid modifier of nanoparticles with polar functional groups of PVB. The presence of these phases highlights the non-miscibility of plasticized PVC with PVB.

Thermal degradation of composites

Thermal stability of all blends and composites has been investigated by thermogravimetry coupled with mass spectrometry and FTIR spectroscopy simultaneously. Table 1 summarizes the onset degradation temperatures, and temperatures of HCl release determined by following $m/z = 36$ from MS analysis during TG measurement.

Thermal degradation of plasticized PVC

It is well known that thermal degradation of pristine PVC occurs in two major mass loss steps related to a first dehydrochlorination reaction yielding to hydrogen chloride release and formation of highly reactive polyene sequences which undergoes chain cracking in a final step. However, in the presence of a plasticizer, the main kinetic parameters and temperatures of reactions are commonly changed. For plasticized PVC, a complex multi-step process of the thermal degradation has been highlighted by several authors [28, 29]. They reported that the first region of degradation is most likely associated with migration of plasticizer, first lost from the surface and then from the bulk. More precisely, investigations of the migration of DEHP in PVC under heating by depth analysis using FT-IR spectroscopy lead to the conclusion that depth profiles depend on the stabilisers used [29].

According to our approach, TG curve and its derivative (Fig. 4a) showed that thermal degradation of DEHP-plasticized PVC occurs in three major steps. FTIR (Fig. 4d_1 and d_2) and MS spectra (Fig. 4b) did not highlight a migration of the plasticizer, but evidenced that HCl, released during the first PVC degradation step, quasi-immediately reacts with the plasticizer to hydrolyze it and to form the corresponding monoester (monobenzylphtalate). This result was also been observed by Jackson and Rager [30]. After this reaction, degradation of plasticized PVC occurs similarly to non-plasticized PVC.

Table 1 Onset degradation temperature (T_{onset}) and HCl release temperature (T_{HCl}) of PVC composites, evaluated from thermogravimetric measurements

Sample	T_{onset}/°C	T_{HCl}/°C
Plasticized PVC	205	208
Plasticized PVB	287	/
PVC/10 phr PVB	221	221
PVC/20 phr PVB	227	230
PVC/30 phr PVB	228	235
PVC/40 phr PVB	231	238
PVC/50 phr PVB	238	249
PVC/60 phr PVB	244	253
PVC/70 phr PVB	255	262
PVC/80 phr PVB	271	284
PVC/90 phr PVB	282	/
PVC/3 phr $CaCO_3$	210	215
PVC/5 phr $CaCO_3$	212	220
PVC/8 phr $CaCO_3$	216	226
PVC/10 phrPVB/3 phr $CaCO_3$	222	255
PVC/10 phrPVB/5 phr $CaCO_3$	223	264
PVC/10 phrPVB/8 phr $CaCO_3$	226	267

Thermal degradation of plasticized PVB

Plasticized PVB revealed a two-stage degradation (Fig. 5). At about 240 °C, MS spectra (Fig. 5d_1) evidenced the release of butyraldehyde ($m/z = 72$) immediately followed by elimination of carbon dioxide ($m/z = 44$), acetic acid ($m/z = 60$), benzene ($m/z = 78$), and water ($m/z = 18$). As described by numerous authors, PVB degradation involves elimination of the butyral, acetate and alcohol functionalities present in the polymer [31, 32].

Butyraldehyde elimination has been proposed according an intramolecular mechanism, yielding majoritary to butanal but also to butenal, and dihydrofuran (Scheme 3). The process also creates polyene sequences that subsequently form aromatic compounds by free radical mechanisms.

The main degradation process of vinyl alcohol moities of PVB occurs through a dehydration reaction yielding water release, but can also result in the formation of aldehydes and ketones via free radical hydrogen abstractions (Scheme 4) [33].

The acetate functions are eliminated from the polymer backbone in an autocatalytic reaction (Scheme 5) [34, 35]. This results in the formation of acetic acid ($m/z = 60$) and polyene sequences in which double bonds will catalyze the deacetylation.

Polyene sequences formed by degradation of butyral, hydroxyl, and acetate functions fully degrade at higher temperatures.

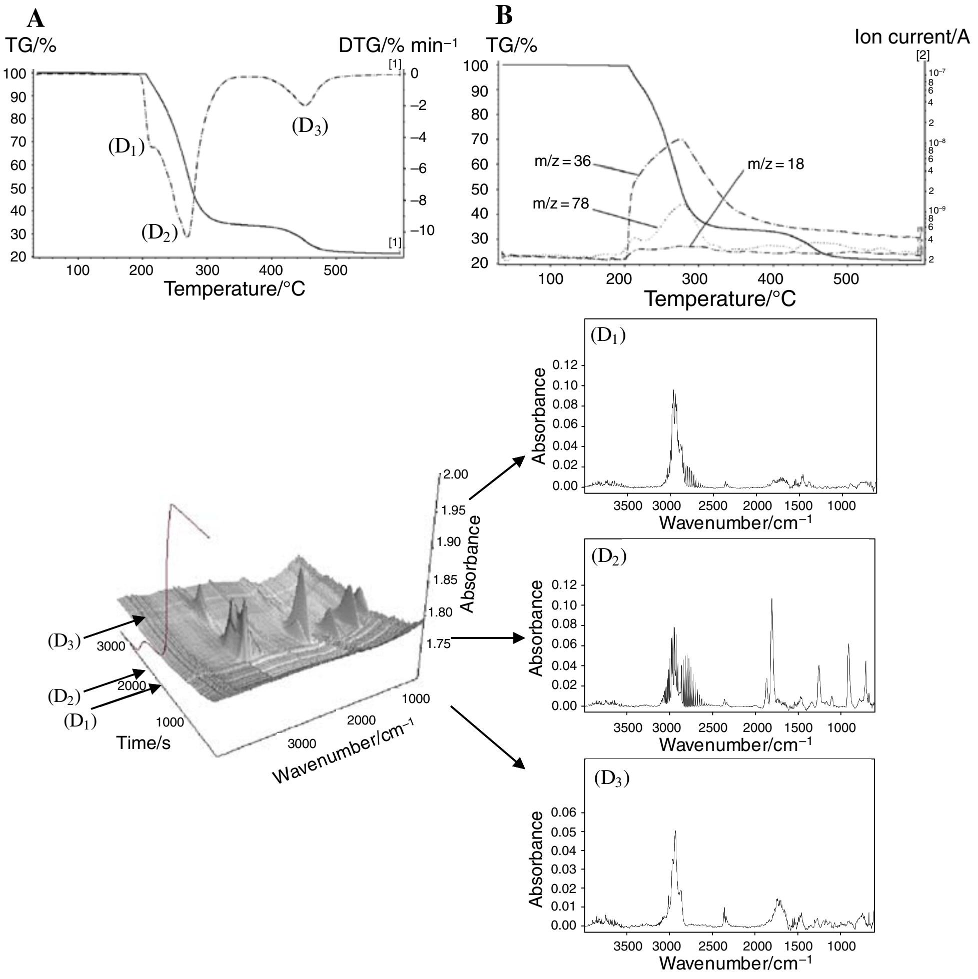
At higher temperature, from 400 °C (Fig. 5d_2), FTIR spectra reveal the volatilization of non-degraded DEHP.

In the following experiment, $m/z = 72$ ion fragment related to butyraldehyde will be considered as characteristic to PVB degradation.

Thermal degradation of plasticized PVC/PVB blends

Influence of PVB content on PVC composite thermal stability has been investigated (Fig. 6 and Table 1). Both a

Fig. 4 Thermogravimetric analysis of plasticized PVC (**a**) coupled with mass spectrometer (**b**), 3D FTIR spectroscopy (**c**), (**d**) exhibits extraction of FTIR 3D spectra during thermal degradation stages



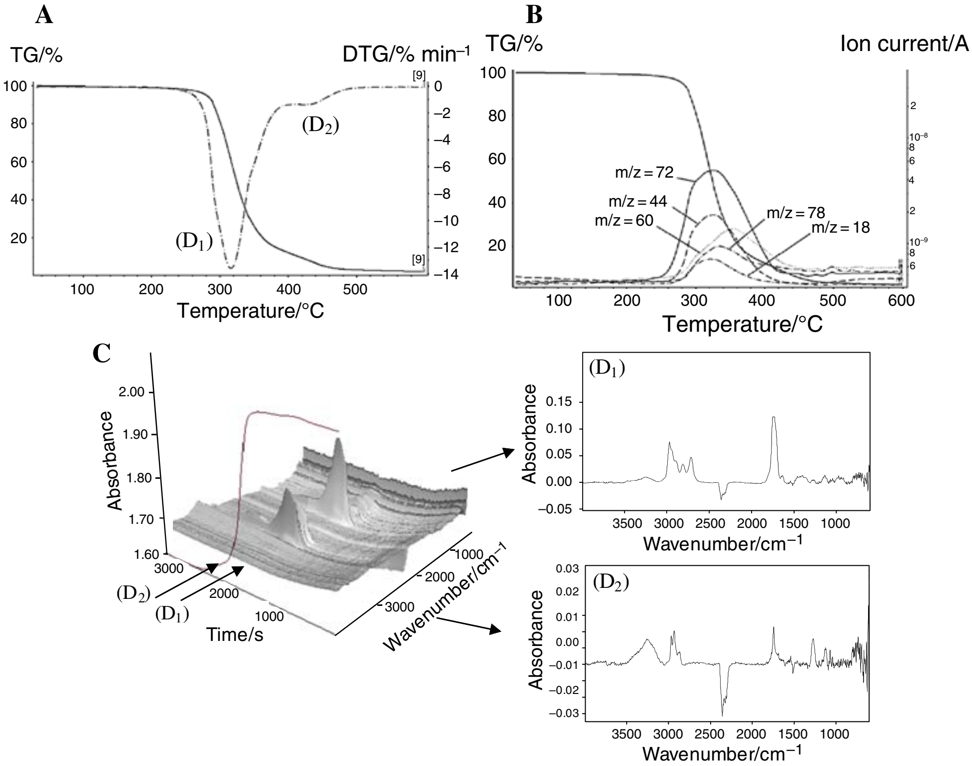
delay of the mass loss (T_{onset}) and the release of HCl (T_{HCl}) have been evidenced with the increase of PVB amount. Moreover, TG curves evidenced a different PVB degradation mechanism in the presence of PVC through a lower PVB moiety degradation temperature and a significantly higher residual mass at the end of blend degradation.

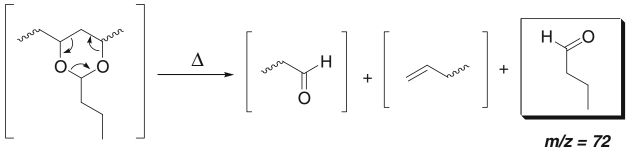
According to the derivative curve of TG, PVC/PVB binary blends (Fig. 7a) exhibited a three main stages degradation. However, analysis of the volatile species evidenced four steps over the range of temperature 200–350 °C. During the first step, that exhibited a high reaction kinetic, MS spectra ($m/z = 72$ on Fig. 7b) and FTIR spectra (Fig. 7d_1) evidenced the degradation of PVB matrix. This step was quickly followed by a second stage involving the degradation of PVB and PVC, highlighted by release of butyraldehyde ($m/z = 72$ on Fig. 7b and d_2), CO_2 ($m/z = 44$ Fig. 7b), H_2O ($m/z = 18$) and HCl ($m/z = 36$ and Fig. 7d_2). Figure 7d_3 showed the subsequent degradation of the plasticizer by reaction with HCl. PVC being the most important polymer in mass, a last stage consisted in only HCl release (Fig. 7d_3). When we compare both onset degradation and HCl release temperatures for plasticized PVC and plasticized PVC containing 10 phr of PVB (Table 1), a stabilizing effect was highlighted. Mohamed et al. reported a stabilizing effect of PVB on PVC degradation by radical substitution of chlorine atoms on PVC chain by PVB, yielding to the release of acetic acid providing from acetate groups elimination [18]. Moreover, they have suggested the HCl trapping by CH_3COOH to form CH_3COCl. In our case, the used PVB contains only 1% of acetate groups, suggesting the contribution of other groups, especially butyral moieties which undergo catalytic acid hydrolysis by HCl leading to simultaneous release of butyraldehyde. However, similar to the previously described PVB degradation reactions, the mechanism can be assumed mainly radical.

Thermal degradation of plasticized PVC/$CaCO_3$ nanocomposites

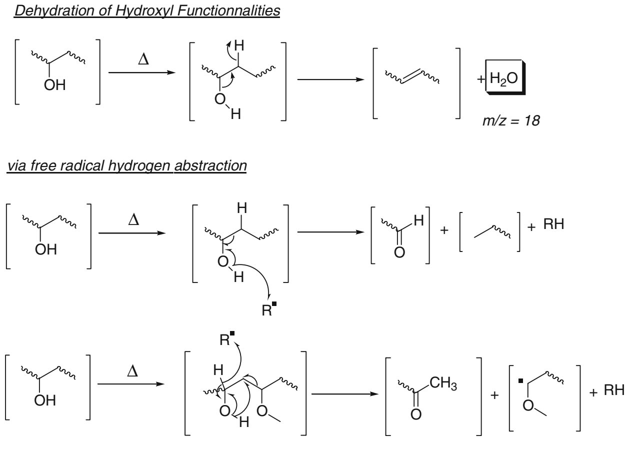
Figure 8 shows the TG curves of plasticized PVC containing $CaCO_3$ nanoparticles. As also reported by Chen et al. [36], a slight delay of onset degradation temperature was evidenced (Table 1) and increased with the nanofillers

Fig. 5 Thermogravimetric analysis of plasticized PVB (**a**) coupled with mass spectrometer (**b**), 3D FTIR spectroscopy (**c**), (**d**) exhibits extraction of FTIR 3D spectra during thermal degradation stages





Scheme 3 Thermal degradation of PVB butyral groups



Scheme 4 Thermal degradation of PVB hydroxyl functions

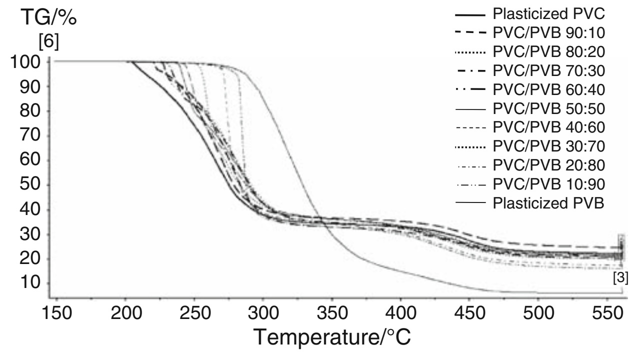
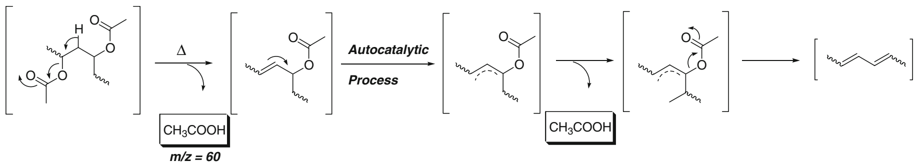


Fig. 6 Thermogravimetric curves of PVC/PVB blends

content. Moreover, following $m/z = 36$ ion fragment by mass spectrometry (Fig. 9b), related to HCl release, highlighted an even more significant delay of the HCl release temperature compared with pristine plasticized PVC. This result evidenced the HCl scavenger effect of the particles during PVC thermal degradation.

Furthermore, in pristine plasticized PVC, chlorine evolves as soon as the degradation process begins (Fig. 6)

Scheme 5 Thermal degradation of PVB acetate functions



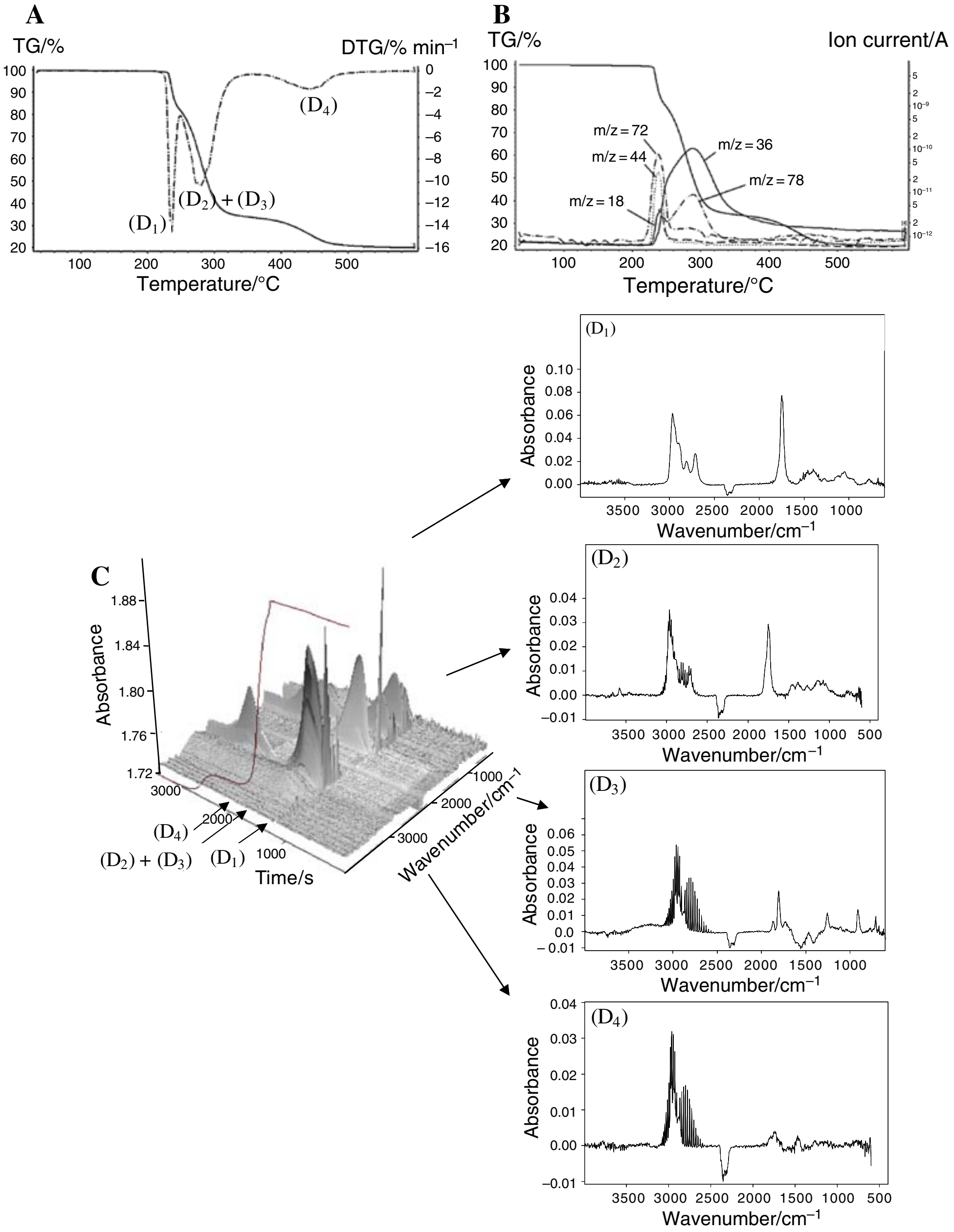


Fig. 7 Thermogravimetric analysis of plasticized PVC/PVB 30 phr (**a**) coupled with mass spectrometer (**b**), 3D FTIR spectroscopy (**c**), (**d**) exhibits extraction of FTIR 3D spectra during thermal degradation stages

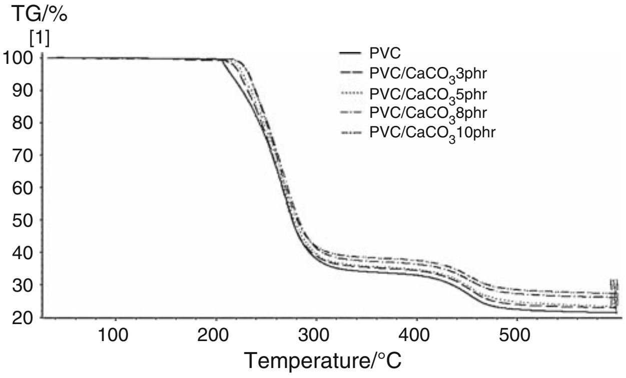


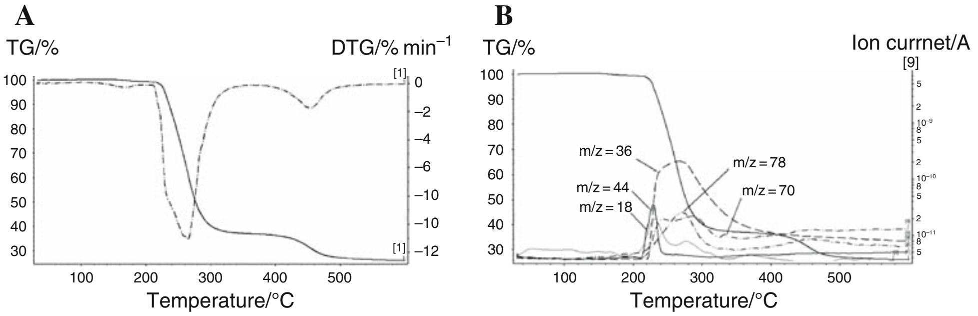
Fig. 8 Thermogravimetric curves of PVC/$CaCO_3$ nanocomposites

whereas in the presence of $CaCO_3$ nanoparticles, HCl is released about 10 °C later. Elimination of HCl was then replaced by carbon dioxide and water (Fig. 9b), as shown by mass spectrometry through $m/z = 44$ and 18 fragments respectively, and by FTIR spectroscopy through vibrations bands in the range of 4,000–3,500 cm^{-1} and 1,600–1,500 cm^{-1} (not shown here). This result evidenced the stabilizing reaction that occurs between nanoparticles and evolved HCl [37–39]:

$$CaCO_3 + 2HCl \leftrightarrow CaCl_2 + H_2O + CO_2$$

This acido-basic process to trap the HCl molecules formed during PVC dehydrochlorination leads to a stabilizing effect on the dehydrochlorination. Moreover, Starnes et al.

Fig. 9 Thermogravimetric analysis of plasticized PVC/$CaCO_3$ (**a**) coupled with mass spectrometer (**b**)



have reported that dehydrochloration autocatalysis involved cation radicals formed by protonation of polyene and polymer chains (Scheme 1) [5]. By trapping HCl and thus the acid proton, $CaCO_3$ particles could act at this level to avoid the subsequent formation of the radical and to limit consequently the degradation catalysis.

Thermal degradation of plasticized PVC/PVB/$CaCO_3$ ternary systems

Effect of incorporation of both previously studied moieties, PVB and $CaCO_3$ nanoparticles, has been investigated with the same methodology (Figs. 10 and 11); results are summarized in Table 1.

As it could be expected, both onset temperature and HCl release were delayed. Moreover, mass spectra showed that chlorine signal shifted significantly by incorporation of both moieties PVB and $CaCO_3$ nanoparticles. The delay is significantly higher than in the presence of one or the other moiety.

In the first step, MS spectra (Fig. 11b) revealed the release of both the $m/z = 72$, 44 and 18 ion fragments, characteristic of the stabilizing process by PVB and $CaCO_3$ respectively. This result, confirmed by FTIR spectra (Fig. 11d$_1$), indicated that these both moieties act as stabilizers at the same time. Secondly, ion fragments of PVB degradation products decreased, corresponding to a total PVB consuming whereas $CaCO_3$ nanoparticles played still the role of HCl scavenger (Fig. 11d$_2$). At this time, HCl lead to degradation of DEHP into MEHP as shown by FTIR spectra (Fig. 11d$_3$).

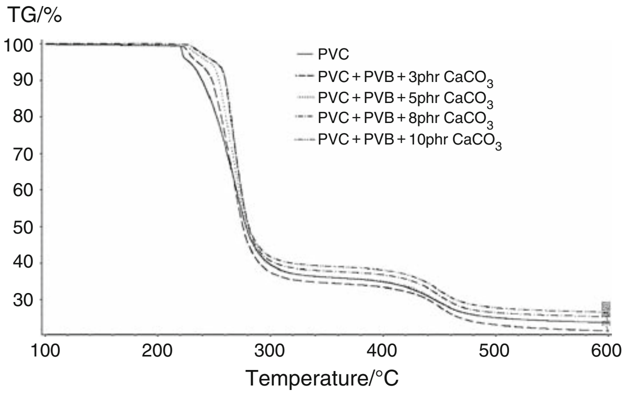


Fig. 10 Thermogravimetric curves of PVC/PVB/$CaCO_3$ nanocomposites

It is important to note that a clear synergetic stabilizing effect on HCl release was obtained when both PVB and $CaCO_3$ nanoparticles were incorporated in PVC. This can be explained by two hypotheses. First, a better dispersion of smaller phases of PVB (Fig. 3a) occurs in the presence of $CaCO_3$ nanoparticles through a viscosity increase of the mixture, yielding to a better shearing efficiency during the elaboration process by melt compounding. The second explanation can be provided by a combined action of these two moieties, with PVB acting according a radical mechanism and $CaCO_3$ particles as acido-basic mechanism. Then, according to the autocatalysis mechanism described by Starnes et al., the release of HCl, the formation of the cation radicals and their reaction should be stabilized. This hypothesis should be highlighted or rejected by investigating kinetic parameters of the first degradation step.

Thermal degradation kinetic

Activation energy of the thermal degradation of plasticized PVC and plasticized PVC containing 10 phr PVB and/or 8 phr $CaCO_3$ was determined for the first degradation step (from 180 to 360 °C) using the Flynn–Wall–Ozawa's method (FWO). This isoconversional method exhibits the main advantage that no knowledge of the degradation mechanisms is required.

The Flynn–Wall–Ozawa isoconversion method [40, 41] uses the equation:

$$\log\beta = -0.457\frac{E}{RT} - 2.315 + \log\frac{ZE}{R} - g(\alpha)$$

where β is the heating rate, E is the apparent activation energy, Z is the preexponential factor, R is the gas constant, $g(\alpha)$ is the kinetic model, and T is the temperature read off from the TG curve for the selected conversion α, where $\alpha = (m_0 - m)/m_0$ (m_0 and m are the initial instantaneous masses).

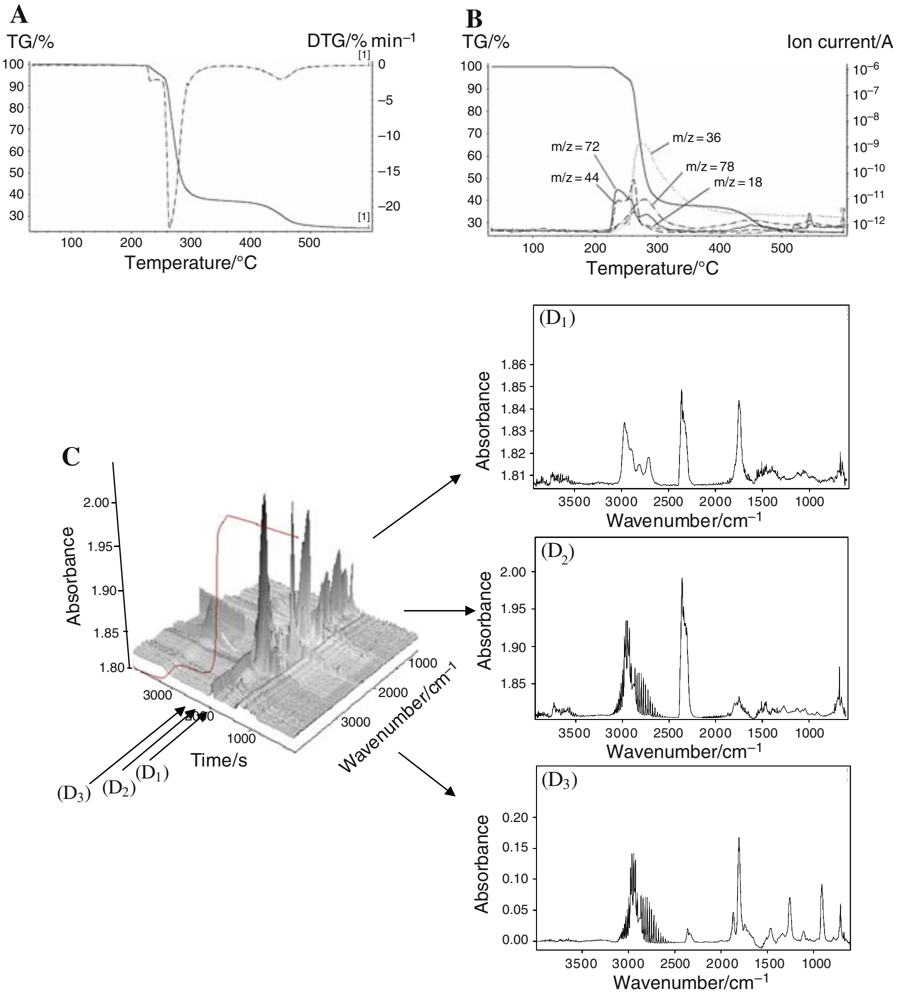


Fig. 11 Thermogravimetric analysis of plasticized PVC/PVB/CaCO$_3$ 100:10:3 (**a**) coupled with mass spectrometer (**b**), 3D FTIR spectroscopy (**c**), (**d**) exhibits extraction of FTIR 3D spectra during thermal degradation stages

Table 2 Values of apparent activation energy (*E*) for the degradation process in the range of 180–360 °C, according to Flynn–Wall–Ozawa theory

Fractional mass loss, α/%	Activation energy, *E*/kJ mol^{-1}			
	PVC	PVC/PVB 10 phr	PVC/CaCO$_3$ 8 phr	PVC/PVB10 phr/CaCO$_3$ 8 phr
0.05	162.19	–	124.05	161.2
0.1	148.78	169.21	179.98	154.44
0.2	148.28	157.27	183.38	182.23
0.3	152.3	156.79	188.21	180.54
0.4	156.28	157.08	191.94	183.49
0.5	160.63	158.43	195.47	184.3
0.6	161.84	158.92	198.9	184.54
0.7	159.4	157.63	199.05	184.01
0.8	154.28	159.59	206.89	182.11
0.9	159.99	171.55	204.22	182.56
0.95	175.27	201.11	210.9	186.29

Applying the isoconversional FWO method on the first degradation rate (180 °C up to 360 °C), and by linear regression analysis, the apparent activation energy was determined as a function of the conversion degree (Table 2) and plotted on Fig. 12. For plasticized PVC, the activation energy curve revealed that *E* is not constant,

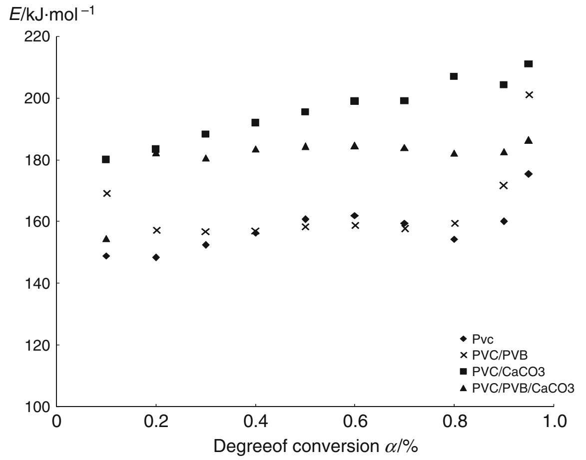


Fig. 12 Plot of activation energy (*E*) versus the reaction rate (α) of plasticized PVC, PVC/10 phrPVB, PVC/8 phr$CaCO_3$, PVC/10 phrPVB/8 phr$CaCO_3$

confirming the presence of several competitive reactions. By incorporation of PVB, the activation energy increased at the beginning of the process, up to $\alpha = 0.4$. For higher values of α (>0.4), the activation energy curve did not show any significant change compared with *E* of PVC. Incorporation of $CaCO_3$ nanoparticles lead to the most important increase of activation energy (about 40 kJ mol^{-1}). However, as unexpected from TG results, and temperatures of HCl release, incorporation of the two stabilizers PVB and $CaCO_3$ did not afford a synergetic stabilization regarding activation energy. Furthermore, blending these stabilizers decreased the stabilization observed with $CaCO_3$ nanoparticles but still increased significantly the stabilizing effect on the first degradation stage compared to PVC and PVC/PVB. All these results should lead to the reject of the hypothesis of a combined action of PVB and $CaCO_3$, as previously envisaged. Furthermore, it may be interesting to compare kinetic results with other isoconversional methods, as ever done by Budrugeac et al. [42, 43]. In their study, similar kinetic values have been obtained for non-plasticized PVC by applying isoconversional methods, such as Friedman and FWO, as well as the invariant kinetic parameters method (IKP). This approach may have a great interest for the composites considered in the present study since they involve several competitive reactions during the first mass loss.

Conclusions

PVB and $CaCO_3$ nanoparticles have been evidenced to be efficient thermal stabilizers for PVC. Coupling thermogravimetric measurements with mass spectrometry and FTIR spectroscopy gave information on the stabilizing mechanism of each moiety.

Both PVB and $CaCO_3$ nanoparticles acted as HCl scavengers and afforded a significant delay of both onset degradation temperature and HCl release. Incorporating these both moieties in plasticized PVC not only lead to a thermal stabilization but also and mostly afforded a synergetic HCl scavenger effect. The HCl release temperature was delayed by about 60 °C by an addition of 10 phr PVB and 8 phr $CaCO_3$ nanoparticles. Moreover, a significant increase of activation energy of the composites has been highlighted by applying Flynn–Wall–Ozawa's model.

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