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THERMAL STABILITY AND MISCIBILITY IN PVC/EVA BLENDS

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Abstract

Thermal stability and degradation processes in PVC/EVA systems were evaluated for a series of EVAs with different vinyl acetate contents. The experimental data revealed a relationship between the thermogravimetric curves and the degree of interaction in the mixtures as compared to the pure polymers, which is consistent with the results of microscopic analysis. Kinetic parameters and lifetime data on the mixtures were also calculated.

Keywords: degradation, kinetic parameters, microscopy, miscibility, PVC/EVA blends, TG

Introduction

Polymer blends have developed very rapidly in the past decade as an efficient alternative to other new materials. Relative to the development of new synthetic processes, this approach takes less time and is more cost-effective. The application of blends is being extensively studied and the material performance is linked to the compatibility of the components. The temperature resistance, i.e. the degradability and the shelf life, must be emphasized because interaction between the components plays a fundamental role. It may accelerate or retard the degradation process [1].
In this work, thermogravimetry (TG) is used to evaluate the effects of specific interactions on PVC/EVA blends, with a kinetic treatment of thermal degradation [2–5].

Experimental

The pertinent parameters of the polymers and experimental procedures are described elsewhere [6].
The degradation experiments and the vinyl acetate (VA) content of the EVA samples were obtained by thermogravimetric analysis with a Perkin-Elmer TGA-7 thermobalance calibrated with alumel (T_c=163°C), nickel (T_c=354°C) and perkalloy (T_c=596°C) standards.

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Results and discussion

The degradation curves exhibit two distinct slopes, which are characteristic of the blend decomposition. The first is attributed to PVC dehydrochlorination or to EVA deacetylation. The second shows the region where polyenic units formed in both polymers in the first reaction are degraded. Although PVC and EVA behave similarly, the degradation of the first begins at lower temperature. Figure 1 shows a typical set of thermogravimetric curves of PVC and EVA for various heating rates. The lower the rate, the greater the degradation.

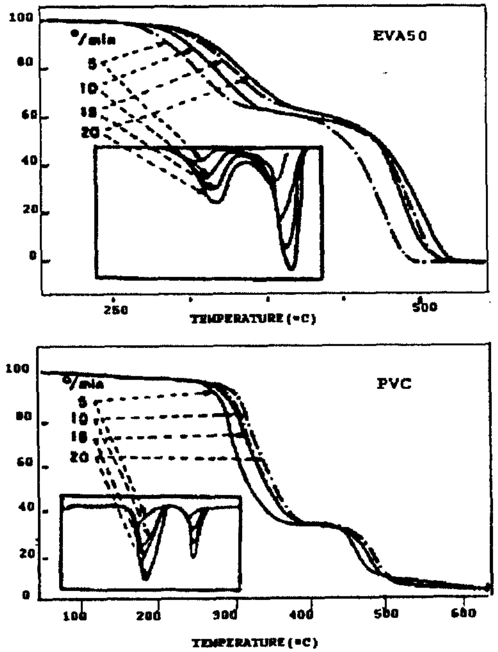


Fig. 1 TG curves for EVA50 and PVC, obtained at various heating rates (5, 10, 15 and 20°C min^{-1})

The acetate content of the copolymers was determined by quantification of the acetic acid evolved from the first degradation. The values obtained agree with the elemental analysis, as shown in Table 1.

Thermal degradation reactions can be divided into two main steps. The first is depolymerization, occurring in the main chain. It alters the chemical nature of repetitive units. In sequences that contain VA units, the ester is decomposed, releasing acetic acid. The double bonds generated in the main chain tend to produce conjugation. PVC and EVA undergo two kinds of reaction. In order to evaluate the degradation parameters, the same sample was investigated at different heating rates, i.e. 5, 10, 15 and 20°C min^{-1}. Two conversions (percentage mass loss) were selected for each region. The initial step was monitored at conversions of 10 and 20%; the second step was monitored at 75 and 85%. PVC/EVA blends degrade like

Table 1 Acetate content in EVA copolymers (w/w%)

Sample	Nominal	Obtained	
		Elem. anal.	TG
EVA31	31	34.7	31.5
EVA41	41	42.3	41.2
EVA45	45	46.9	45.2
EVA45A	45	46.2	45.6
EVA50	50	53.5	52.4
EVA70	70	72.4	69.3

the pure polymers. PVC dehydrochlorination and EVA deacetylation occur in the same temperature region. This prevents the quantitative determination of the components of the blends, as shown for PVC/EVA50 mixtures.

The blends also have the same initial degradation region and it is not possible to distinguish the degradation of the individual components. This happens independent of the acetate content in the copolymer. In both degradation regions, the individual curves of the components coalesce. The derivative curves show that for EVA compositions higher than 30% a temperature displacement appears at the beginning of decomposition. This indicates an apparently high thermal stability.

Degradation in polymer blends can be inhibited or accelerated. The phenomena that occur in these mixtures are frequently attributed to by-products evolved from the degradation of one or both components in the blend. In PVC mixtures, the liberation of HCl plays the main role. Free radicals are also formed in this process [8–14]. The by-products of one component can catalyse the degradation of the other component. This is known as an autocatalytic reaction. To observe autocatalytic degradation in a blend, the mass loss variation at one temperature was compared with the expected temperature calculated by the additivity law.

It was observed for PVC/EVA70 and PVC/EVA50 blends that, even with similar shape, the curves display differences in the first degradation region for low acetate content. The variation in conversion in these blends diminishes as the copolymer content in EVA rises.

The effect observed before can be maximized by registration of the maximum conversion variation rates $(dC_1/dt)_{max}$ and $(dC_2/dt)_{max}$. These correspond to the first and second degradation regions registered from the TG derivative curves for PVC/EVA50 and PVC/EVA70 blends (Fig. 2). These curves exhibit distinct behaviour. The values of $(dC_1/dt)_{max}$ diminish with increase of the EVA50 composition to 30% of the copolymer. Beyond 30% EVA, the curves reach a plateau.

PVC/EVA70 blends show that the conversion variation rate slowly rises and stabilizes at 50% EVA content. However, when its proportions are compared, these correspond to a similar molar acetate concentration. This suggests the existence of a critical concentration of the acetate content in the mixture, above which the maximum conversion rate of both degradation regions does not increase.

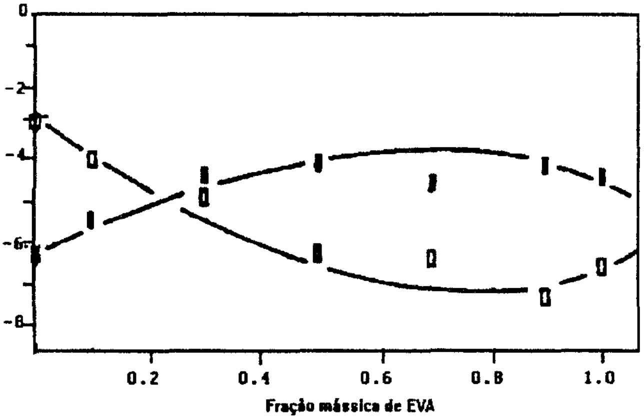
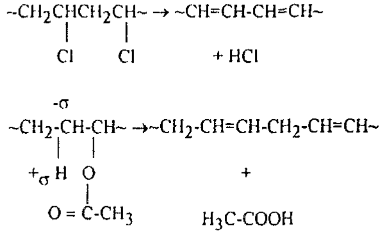


Fig. 2 Variation of the maximum conversion rates at first stage $(dC_1/dt)_{max}$ and at the second stage $(dC_2/dt)_{max}$, of degradation for PVC/EVA50 and PVC/EVA70 blends as function of composition. ▲ 1^a degradation region; ■ 2^a degradation region

These degradation results were very much higher than those obtained for the PVC/polyvinyl acetate (PVA) blends, although in some cases the quantity of acetate available to generate acetic acid is significatively lower than in the homopolymer blend [8–19]. This may be explained by the miscibility of the components. The size of the phase domains in the PVC/PVA system is of the order of 30 μm. This indicates that this is an immiscible blend.

The data were correlated with the size of the domains by transmission electronmicroscopy. PVC/EVA50 and PVC/EVA70 blends showed domains of 100 nm [18]. A high degree of miscibility is observed in these systems.

The interactions in polymer blends occur at the interface between domains of the components or by diffusion of low molecules or radicals formed from one of the components. These can migrate across the interface in order to react with the other component [19]. Acid catalysis takes place in PVC/PVA mixtures due to the formation of HCl from PVC that migrates to the PVA domain. Its presence can catalyse the deacetylation reaction. The same effect occurs when the acetic acid reaches the PVC-rich phase through dehydrochlorination [15] as follows:



$$\sim CH_2\underset{\underset{Cl}{|}}{C}HCH_2\underset{\underset{Cl}{|}}{C}H\sim \rightarrow \sim CH{=}CH\text{-}CH{=}CH\sim \; + HCl$$

$$\sim CH_2\text{-}\overset{-\sigma}{\underset{\underset{+_{\sigma}H}{|}}{C}}H\text{-}\underset{\underset{O=C\text{-}CH_3}{\underset{|}{O}}}{C}H\sim \rightarrow \sim CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\sim \; + H_3C\text{-}COOH$$

In this way, the diffusion of degradation products such as HCl and acetic acid that catalyse deacetylation and dehydrochlorination, respectively, is facilitated. This oc-

Table 2 Mass loss (%) obtained by thermogravimetric analysis of PVC/EVA70 blends

Sample	Mass fraction	Heating rate/ °C min^{-1}	Degradation temperature/°C First stage 10%	20%	Second stage 75%	85%
EVA7019	0.9	20	338	359	488	495
		15	332	353	483	489
		10	321	339	471	478
		05	303	319	461	471
EVA7037	0.7	20	325	344	415	492
		15	323	341	485	492
		10	309	326	476	485
		05	303	321	466	473
EVA7055	0.5	20	329	345	485	495
		15	323	339	480	488
		10	314	330	475	484
		05	307	323	465	472
EVA7073	0.3	20	320	337	487	498
		15	318	334	482	493
		10	305	321	472	484
		05	288	305	465	479
EVA7091	0.1	20	308	319	485	500
		15	307	320	485	500
		10	299	310	469	482
		05	280	289	467	481

curs if the system has small domains characteristic of semi-miscible or miscible mixtures. Therefore, the higher degradation of the PVC/EVA blends is justified.

In order to evaluate the kinetic parameters as a function of blend composition, a series of thermogravimetric tests were performed at different compositions and heating rates. Table 2 shows the degradation temperatures of PVC/EVA70 blends for each degradation region. Again, increase of the heating rate elevated the decomposition temperature for every region or composition.

The kinetic parameters were also calculated for other PVC/EVA pairs with stoichiometric compositions at different heating rates. Table 3 shows that the influence of the heating rate is the same as previously. The first degradation region was regarded as the more significant region to express the degradation process in PVC/EVA blends.

Thermal degradation reactions can be divided into two main steps. The decomposition reaction that occurs in the main chain alters the chemical nature of repetitive units. In sequences that contain VA units, the ester is decomposed, with splitting-off of acetic acid. The double bonds generated in the main chain induce a propagation

Table 3 TG data for PVC/EVA blends at stoichiometric compositions

Sample	Degradation temperature				
	Heating rate/ °C $\min^{-1}$	First stage		Second stage	
		10%	20%	75%	85%
EVA45	20	316	339	496	498
	15	309	329	484	492
	10	302	325	428	485
	5	291	311	470	478
EVA45A	20	298	323	485	493
	15	294	318	484	492
	10	295	321	489	488
	5	283	307	467	474
EVA41	20	266	303	482	495
	15	274	306	483	491
	10	258	289	422	486
	5	244	275	466	473
EVA31	20	306	332	488	495
	15	301	329	490	497
	10	289	316	480	487
	5	277	306	470	478

Table 4 Activation energies, E, and times to fail, t_f, at 200°C for pure PVC and EVAs

Polymer	E/kJ mol^{-1}	t_f/h
EVA31	144	23.704
EVA41	141	16.338
EVA45	140	12.465
EVA50	124	5.470
EVA70	100	1.240
PVC	113	2.850

mechanism that produces conjugation. The reference temperature of 200°C and a conversion of 10% were used for an expression of the time to fail. Table 4 lists activation energies and times to fail for the pure polymers. It can be observed that E and t_f decrease as the acetate content in the copolymer is increased. PVC has an E near the EVA70 value, but with higher t_f.

The blend composition effect on E and t_f was studied for PVC/EVA70 mixtures, as shown in Table 5. It can be observed that the addition of PVC promotes a reduction in the activation energy of degradation and the time to fail. The thermal stabilities of the blends are lower than those of the pure polymers.

Table 5 Activation energies, E, and times to fail, t_f, at 200°C for PVC/EVA70 mixtures

Blend	Mass fraction	E/kJ mol^{-1}	t_f/h
EVA7019	0.1	102	565
EVA7037	0.3	98	316
EVA7055	0.5	128	1560
EVA7073	0.7	96	246
EVA7091	0.9	88	123

Table 6 Activation energies, E, and times to fail, t_f, at 200°C for different stoichiometric PVC/EVA70 mixtures

Blend	Mass fraction	E/kJ mol^{-1}	t_f/h
PVC/EVA70	0.5	128	1.560
PVC/EVA50	0.5	133	1.774
PVC/EVA45	0.5	148	1.607
PVC/EVA41	0.5	94	40
PVC/EVA31	0.5	116	312

When the influence of the acetate content in the copolymer is considered, it must be borne in mind that, as the acetate content increases, the miscibility of the blend also increases. Table 6 shows the E and t_f values for different PVC/EVA mixtures at stoichiometric compositions. It may be noted that the blends with higher acetate content in the copolymer, e.g. EVA45, EVA50 and EVA70, have higher E and t_f than those of the EVA31 and EVA41 blends. Similar values at high acetate contents are probably explained by intermolecular interactions [18]. This acts as a retardation agent for blend degradation. Similar values appear for the EVA45, EVA50 and EVA70 blends, due to the error propagation in the calculation of these parameters. This does not permit data comparison between the blends. Again, all blends displayed more degradation than expected for the pure polymers.

Conclusion

Thermogravimetry applied to PVC/EVA blends permitted a degradation study. It was verified that, as in other systems, the decomposition curves of blends and pure polymers are different. The decomposition temperature of pure EVA increases as the heating rate is raised. The contrary effect is observed when the acetate content is increased. Similar effects occur in the blends. All blends showed autocatalytic effects that increase the degradability. The activation energies and times to fail of the blends were presented. It could be observed that the extreme compositions exhibited less stable behaviour. In the more miscible pairs, the possible autocatalytic effects are balanced by the intermolecular interactions that can retard the dehydrochlorination and deacetylation reactions.

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