

Blends of polyolefins and semiflexible liquid crystalline polyesters.

Part 1. Thermogravimetric analysis ¹

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Abstract

The thermal stability of blends consisting of polyethylene (PE) or isotactic polypropylene (PP) with two different semiflexible liquid crystalline polyesters (LCP) was analysed by thermogravimetry (TG) under nitrogen and air atmospheres. The effects of the structural parameters of the LCP and of its content in the blends were evaluated.

The temperatures at which degradation starts indicated that the stability of the mixtures is governed by the presence of the less stable component, under the experimental conditions applied. Comparison between predicted and experimental weight losses versus temperature support speculations on polymer–polymer interactions in the blends.

INTRODUCTION

Thermotropic liquid crystalline polymers belong to a class of materials that yields anisotropic melts of relatively low viscosities [1, 2]. This behaviour plays a key role in defining the properties of polymer blends consisting of a conventional or engineering thermoplastic and an LCP component [3–5]. In consequence, the processing temperatures of the blends appear to be lower than those required for the processing of the pure matrices. The end products are reinforced by inherent fibrillation of the LCP and upgrading of the overall mechanical properties of the dispersant matrix. So far, however, very little detailed work has referred to the thermal stability of blends containing LCP [6, 7]. In addition to the rheological benefits achieved in the processing of LCP-containing polymer blends, the

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² In memoriam.

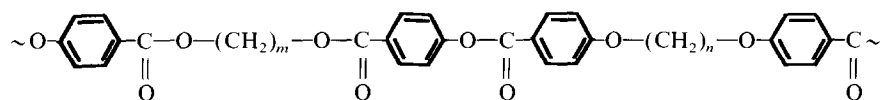
thermal stability must be evaluated in order to develop a better performance profile of the final products.

The present paper reports an investigation of the thermal stability of blends consisting of high-density polyethylene (PE) or isotactic polypropylene (PP) as the continuous dispersant matrix and thermotropic liquid crystalline polyesters based on linear aromatic diads or triads interconnected by polymethylene segments, as a second component.

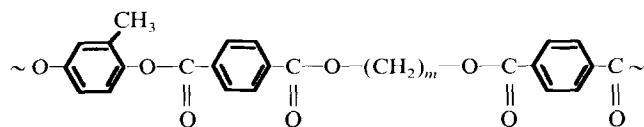
EXPERIMENTAL

Materials

The blend matrices were high-density polyethylene (PE) supplied by EniChem and commercially available isotactic polypropylene (PP). The samples of semiflexible liquid crystalline polyesters (LCP) belonging to the series named $C_m C_n$ and C_m were made available by the LC research groups of the University of Bologna [8] and University of Pisa [9]. They are, respectively, based on 4,4'-alkylene dioxydibenzoic acids and α,ω -alkylene di-4-hydroxybenzoate ($C_m C_n$), and methyl hydroquinone and α,ω -(bis-terephthaloyloxy)alkylene (C_m).



$C_m C_n$ $m = 10$; $n = 6, 7, 9$



C_m $m = 10, 12$

Some characteristics of the polymer samples utilized in the present investigation are listed in Table 1.

Preparation of the polymer blends

The polyolefin/LCP blends were prepared by dissolving the polymer samples in *o*-xylene. The overall solid concentration was 2% wt./vol. at any different polyolefin/LCP ratio. The stirring time was 1 h under nitrogen flow at 125°C in all cases. The polymers were coprecipitated in ethanol as non-solvent, in excess of 10:1 with respect to *o*-xylene, filtered, washed with ethanol, dried at 35°C under reduced pressure for at least 24 h, and stored at ambient conditions.

TABLE 1
Characteristics of the polymer blend components

Material	\bar{M}_w	\bar{M}_w/\bar{M}_n	$T_m/^\circ\text{C}^a$	$T_{N-1}/^\circ\text{C}^b$	$X\%^c$
PP	280000	–	164	–	50.3 ± 1.4
PE	96000	7.1	131	–	83.9 ± 5.5
C ₁₀ C ₆	19000	2.0	186	214	–
C ₁₀ C ₇	19000	1.8	151	184	–
C ₁₀ C ₉	15000	2.9	149	180	–
C ₁₀ A	24000	2.3	158	193	–
C ₁₀ B	65500	2.7	162	213	–
C ₁₂	61600	2.6	160	190	–

^a Melting temperature recorded on the polymer samples after precipitation from solution.

^b Nematic–isotropic phase transition. ^c Degree of crystallinity evaluated by DSC for the polymer samples precipitated from solution. Heat of fusion values of 209 J g⁻¹ for PP and 277.1 J g⁻¹ for PE [10] were taken as reference values.

Thermogravimetric analysis

Thermogravimetric curves were obtained from the Mettler TA4000 Thermal analysis system equipped with a TG50/M3 thermobalance and recorded by means of a Graphware TA72. The experiments were carried out in dynamic scanning mode from 50 to 650°C in nitrogen and air atmospheres (200 ml min⁻¹), at a heating rate of 10°C min⁻¹. The weight of the analysed samples was in the range 3–5 mg.

RESULTS AND DISCUSSION

The derivatives of the TG curves will be considered first because they tend to emphasise changes in the signal profile of the overall weight loss.

Blends of polyolefins with C_m LCP were analysed by dynamic thermogravimetry at three different polyolefin/LCP weight ratios: 90/10, 80/20 and 70/30. Figures 1 and 2 show the trends of the temperature of decomposition T_{di} recorded under nitrogen and air, respectively, for the polymer blends based on PE or PP with two C_m LCP samples containing 10 and 12 carbon atoms in the flexible spacers. The T_{di} values of the blends decreased with increasing LCP concentration in the case of experiments performed under nitrogen atmosphere. Under air atmosphere, an overall drop of about 150°C with respect to previous conditions was detected in the polyolefins and their blends with LCP, whereas the stability of the LCP homopolymers was very little affected.

Under nitrogen atmosphere, the polyolefins and the relevant blends are more stable than the C_m LCP. Hence, the decomposition of the blends appears to be governed by the LCP behaviour. The apparent higher stability

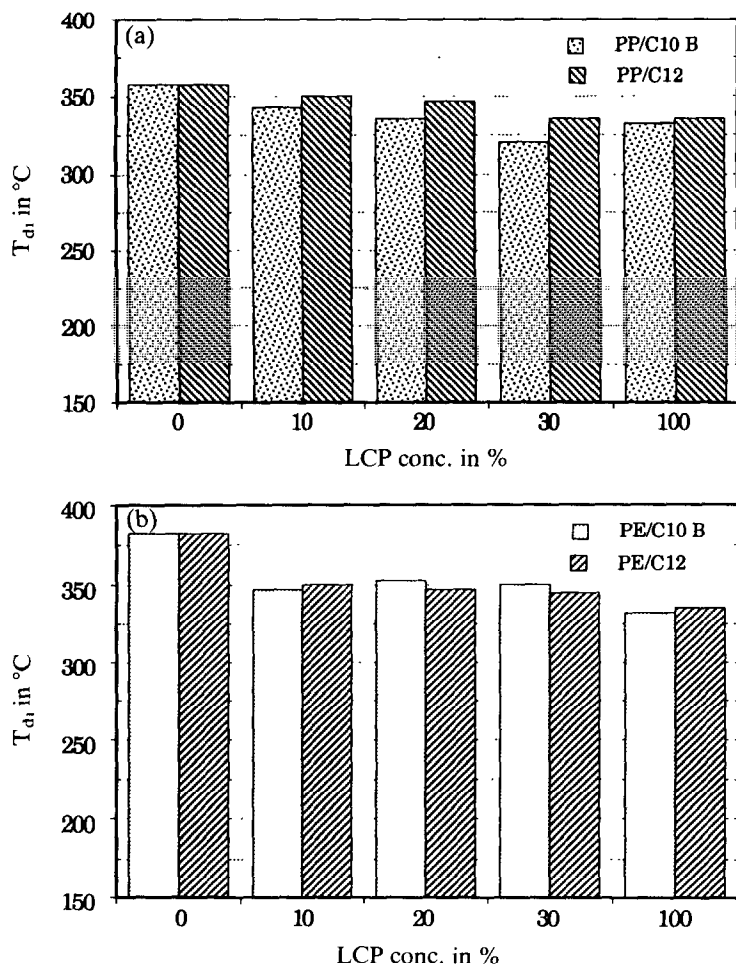


Fig. 1. Degradation temperature T_d under nitrogen atmosphere as a function of the size of the flexible spacers and the LCP content for: (a) PP blends; (b) PE blends.

in the blends of the LCP component with respect to the corresponding pure material, may be connected with some stabilising dilution effect exerted by the more stable polyolefin component. This consideration can be substantiated by two facts derived from analysis of the different TG profiles reported in Figs. 3 and 4: the derivative peak of the blends at about 400°C tends to overlap that of pure C_m LCP when its concentration increases; the maximum of the derivative peak at about 460°C, corresponding to polyolefin decomposition remains constant.

A behaviour analogous to that observed under nitrogen atmosphere was detected by Metha and Isaye [6] for PEEK/Vectra blends, under air atmosphere. This mixture proved to be incompatible, the LCP being less stable than the dispersant PEEK matrix. These results may indicate that when there is no interaction between the blend components, the T_{di} values

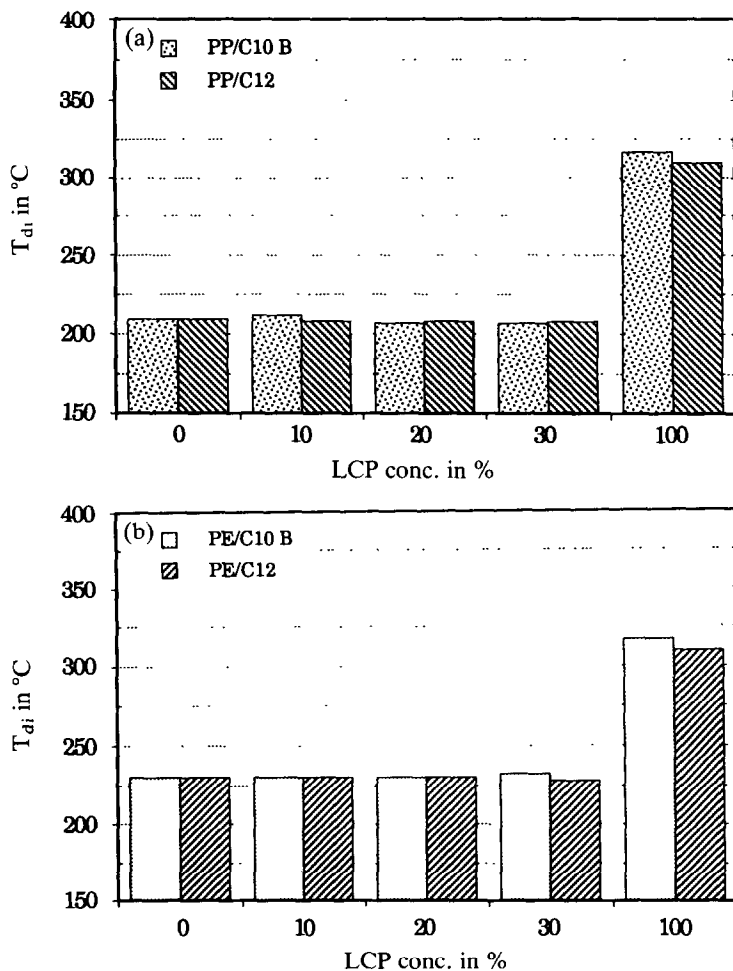


Fig. 2. Degradation temperature T_d under air atmosphere as a function of the size of the flexible spacers and the LCP content for: (a) PP blends; (b) PE blends.

are primarily affected by the less stable component and its concentration in the blend.

When the experiments were carried out under air atmosphere, more complex TG curves were observed that were very similar to typical profiles of pure polyolefins (Figs. 5 and 6). The stability of the LCP was higher than for the polyolefin matrices but slightly lower than that observed under nitrogen atmosphere. Accordingly, it can be stated that the matrix degradation is responsible for the stability of the blends, at all compositions within the range investigated.

The size of the flexible spacers of the C_m polyesters, in spite of their slight differences, appears to impart a distinct character to each mixture when analysed under nitrogen atmosphere. The PP/C₁₂ blends are 15 °C more

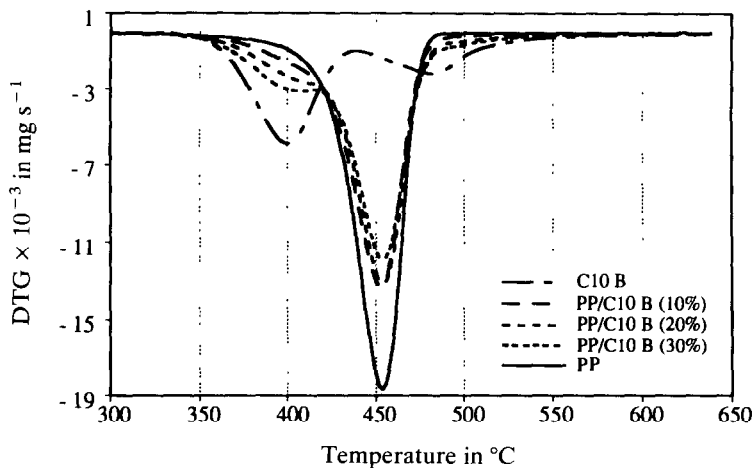


Fig. 3. Derivative TG curves for the decomposition of PP/C10 B blends as a function of LCP content under N_2 atmosphere.

stable than PP/C₁₀. However, in the PE-based blends, the C_m polyesters exhibit a response more similar to the pyrolysis process, with the PE/C₁₀ blend displaying a stability that was slightly higher (about 5°C).

To restrict the number of variables, further investigation of the behaviour of the blends was limited to samples with 30 wt.% of LCP.

In Tables 2 and 3, the initial degradation temperatures were taken either at the beginning of the weight loss on the time–temperature curve (derivative curve, T_{di}) or at the intercept of the tangent extrapolated from the baseline and the lateral weight-loss curve, generally referred as the onset

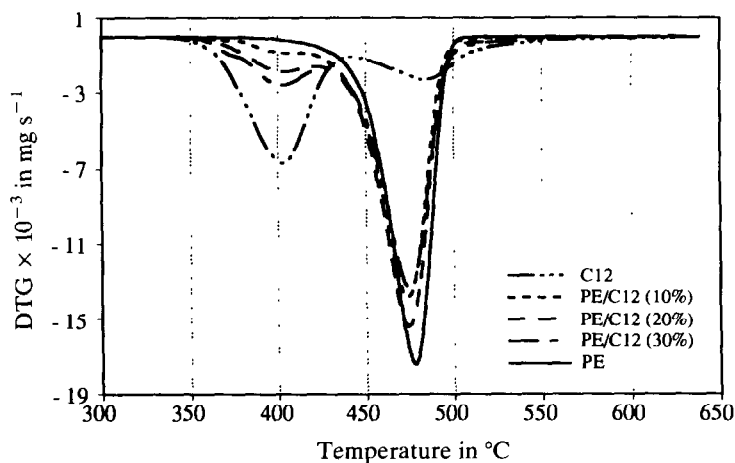


Fig. 4. Derivative TG curves for the decomposition of PE/C12 blends as a function of LCP content under N_2 atmosphere.

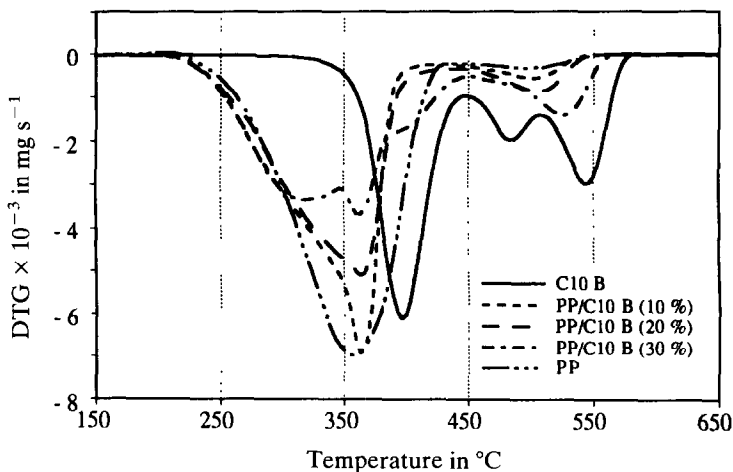


Fig. 5. Derivative TG curves for the decomposition of PP/C10 B blends as a function of LCP content under air atmosphere.

temperature (integral curve, T_{do}). In this respect, the interpretation of the sample behaviour as a function of the LCP structural parameters can be different. In order to rule out any inaccuracy connected with the different kinetic decomposition profiles, the analysis of the results reported here are based on the decomposition temperatures taken from the derivative curves.

The observations reported above for the inert atmosphere decomposition of C_m -LCP-based blends are also valid for blends containing $C_m C_n$ LCP (see Table 2). The two kinds of LCP were less stable than the polyolefin matrices and the blends had an intermediate stability. The mixtures based on PP

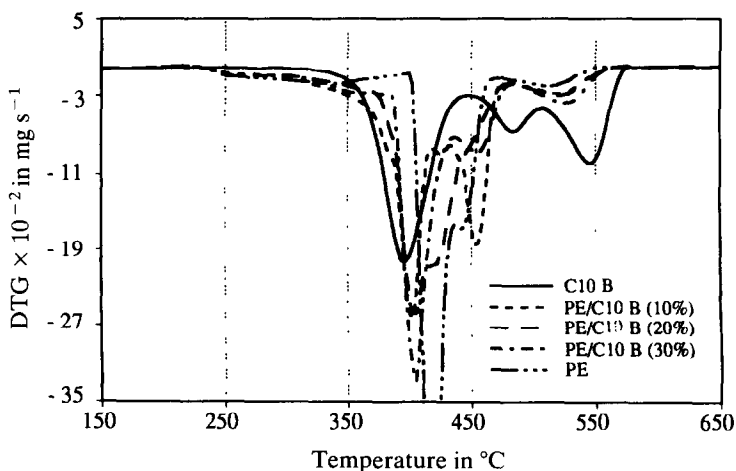


Fig. 6. Derivative TG curves for the decomposition of PE/C10 B blends as a function of LCP content under air atmosphere.

TABLE 2

Degradation temperature T_{di} in °C under N_2 atmosphere for polyolefin/LCP blends with 30 wt.% of LCP. Mean values of 2–6 measurements

	PP	PE	C ₁₀ C ₆	C ₁₀ C ₇	C ₁₀ C ₉	C ₁₀ A	C ₁₀ B	C ₁₂
Initial ^a								
PP	347	–	343	330	349	334	320	329
PE	–	388	335	320	335	332 ± 0	350	345
C _m C _n	–	–	332	315	333	–	–	–
C _m	–	–	–	–	–	314	331	334
Onset ^b								
PP	434	–	423	418	426	381	372	376
PE	–	459	397	384	409	376	379	379
C _m C _n	–	–	392	387	397	–	–	–
C _m	–	–	–	–	–	379	377	379

^a At the initial deviation of the derivative curve. ^b At the extrapolation onset of the integral curve.

displayed T_{di} values fairly close to that of PP, whereas larger decreases in T_{di} values were detected in PE-based blends. This behaviour can be associated with the thermal stability difference between the components of the blends. Studies of the thermal degradation of blends of PE and PP with vinyl polymers [11, 12] demonstrated a lowering of the T_{di} values of the polyolefins due to a radical reaction promoted by a degraded species of the vinyl polymer, which is less stable. The responses at elevated temperatures of the systems

TABLE 3

Degradation temperature T_{di} in °C under air atmosphere for polyolefin/LCP blends with 30 wt.% of LCP. Mean values of 2–6 measurements

	PP	PE	C ₁₀ C ₆	C ₁₀ C ₇	C ₁₀ C ₉	C ₁₀ A	C ₁₀ B	C ₁₂
Initial ^a								
PP	201	–	177	164	176	213	207	208
PE	–	222	217	223	220	233	232	228
C _m C _n	–	–	277	280	272	–	–	–
C _m	–	–	–	–	–	294	320	310
Onset ^b								
PP	277	–	244	250	273	264	267	265
PE	–	255	232	240	236	326	302	313
C _m C _n	–	–	379	381	383	–	–	–
C _m	–	–	–	–	–	373	373	372

^a At the initial deviation of the derivative curve. ^b At the extrapolation onset of the integral curve.

under investigation, as a function of composition, indicate that other factors contribute to the thermal stability of the polyolefin-based blends.

The two kinds of LCP have similar T_{di} values under nitrogen atmosphere, but their values are higher for PP/ $C_m C_n$ blends than PP/ C_m blends. However, the blend with $C_{10}C_7$ polyester appears to be less stable, with an apparent lower T_{di} (315°C) of the LCP homopolymer. In the case of PE/LCP blends, the thermal stability of the PE/ C_m blends is better than that of PE/ $C_m C_n$ blends. The system with $C_m C_n$ did not indicate significant differences between blends and pure LCPs, unlike the case for blends and C_m polymers.

Thus far, it has been established that the thermal stability of the investigated blends is defined by the less stable component and that there is a dilution effect on the stability of the LCP apparently imparted by the polyolefin matrix. However, the behaviour of PE/ $C_m C_n$ blends suggests that other factors are involved. Under nitrogen atmosphere, a pyrolytic process occurs. If the less stable component of the blend exhibits thermolysis at higher temperatures than in the pure state, this signifies that the second component acts as a diluent or a “thermal barrier”. As a hypothesis, one may envisage the formation of an intimate melt mixture. Therefore, the absence of marked changes in the T_{di} of PE/ $C_m C_n$ with respect to the corresponding LCP component, strongly supports the possibility of formation of a poor dispersion of the LCP in the melt matrix; thus, a slight skin protection of the less stable polymer component by the more stable one should take place.

In blends based on C_{10} samples of different molecular weight, an increase in the thermal stability with increasing molecular weight is only detectable with polyethylene-based blends.

The behaviour of pure polymers under air atmosphere indicates the lower stability of polyolefins with respect to the LCP. The thermal oxidation of the blends takes place at the same level as the pure polyolefins. The C_m LCP component seems to have a slight stabilisation effect on both polyolefins whereas a marked destabilisation is observed in PP-based blends containing $C_m C_n$ LCP. A drop of 25–35°C in the stability of the blend with respect to the polypropylene is observed (Table 3). Because the LCP samples are more stable than the polypropylene, the destabilisation of the blend cannot be associated with any chemical reaction resulting from the LCP decomposition. A physical structure modification of PP that favours the thermo-oxidation can therefore be inferred. This is indeed supported by the similarity between the T_{di} values and the mesophase transition ranges. Again, there is no indication that the size of flexible spacer in either LCP influences the thermal stability of the polymers.

It has been shown that the behaviour of blends on heating at elevated temperatures is determined either by the level of dispersion in the melted mixture or by a possible physical modification of one component induced

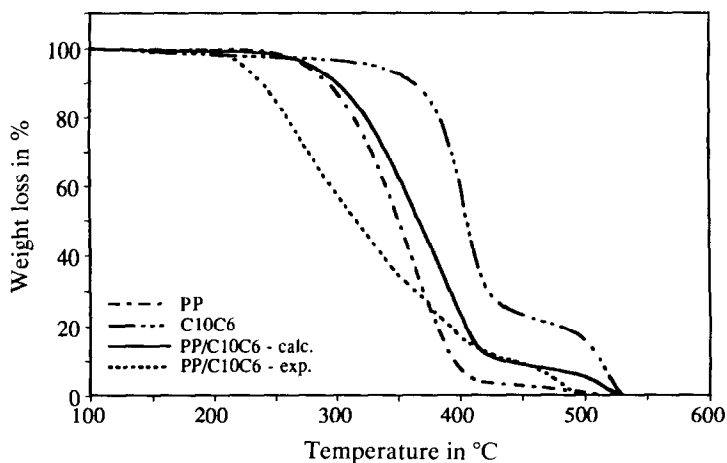


Fig. 7. TG curves for PP, $C_{10}C_6$ and PP/ $C_{10}C_6$ blend (30 wt.% $C_{10}C_6$). Predicted and experimental curves for blends under air atmosphere.

by the presence of the other component. In order to gain a better understanding of this phenomenon, a comparison was made for a mixture containing 30 wt.% LCP, between the integral curve drawn by the additivity rule, assuming an absence of any interaction between the components, and that recorded experimentally (Figs. 7–9).

As shown in Fig. 7, the weight loss of PP/ $C_{10}C_6$ blend, under air atmosphere, behaves differently from that predicted by the additivity rule, exhibiting a stability lower than that of the pure polyolefin. The same trend was detected for all PP/ C_mC_n and PP/ C_m blends, the difference being,

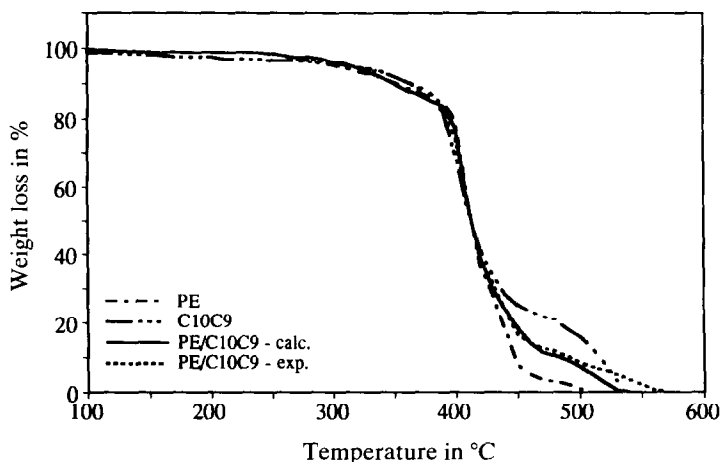


Fig. 8. TG curves for PE, $C_{10}C_9$ and PE/ $C_{10}C_9$ blend (30 wt.% $C_{10}C_9$). Predicted and experimental curves for blends under air atmosphere.

however, less pronounced for the blend containing the C_{10} sample of lower molecular weight. In other polymer blends, deviation between the calculated and the experimentally detected integral traces of the thermal decomposition has also been reported [13, 14]. However, in these cases, the polymer blend appeared to be more stable than the less stable component present in the mixture. The behaviour recorded in our systems could, at present, be associated with the mesomorphic character of the LCP component which seems to force the PP macromolecules to assume conformational arrays that are more susceptible to oxidative reaction.

In the thermal oxidation of the PE/LCP blends, the calculated and experimental curves overlapped in all cases, thus confirming the absence of any disrupting mutual interactions between the polymeric components. A typical example of the observed trends is reported in Fig. 8.

Under nitrogen atmosphere the predicted weight loss curves are located at slightly lower temperatures than those of the experimental curves for all PP/LCP blends. This might imply that some “interaction” is taking place between the components. By analysing the thermal stability as a function of blend composition, it can be deduced that the major factor responsible for this is the dilution effect.

PE/LCP blends behave differently, as exemplified in Fig. 9 for PE/ $C_{10}C_9$ blend. The curves overlap up to about 25–30% weight loss. Above that limiting value, the blends are slightly less stable, implying that the pyrolysis of PE began earlier than predicted by the additivity rule. From these observations, the results attained for the degradation temperatures are a consequence of the physical mixing level defining the dispersion of one component in the other.

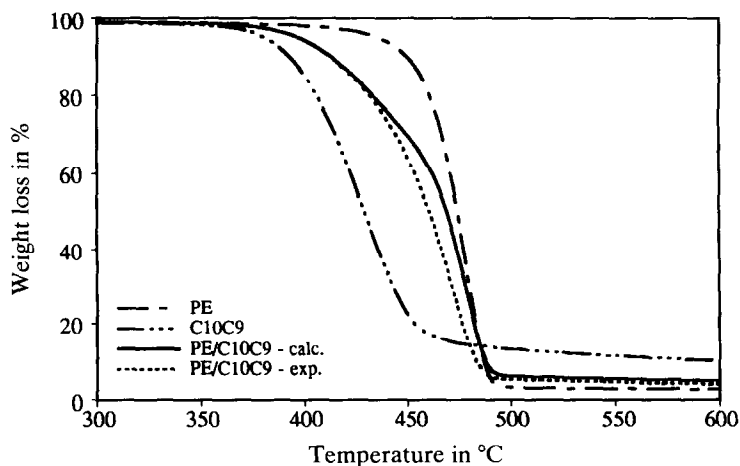


Fig. 9. TG curves for PE, $C_{10}C_9$ and PE/ $C_{10}C_9$ blend (30 wt.% $C_{10}C_9$). Predicted and experimental curves for blends under air atmosphere.

CONCLUSIONS

The thermal behaviour has been investigated of blends based on high-density polyethylene or isotactic polypropylene with thermotropic liquid crystalline polyesters consisting of aromatic diads or triads, interconnected with polymethylene segments of different length. The liquid crystalline polyesters have melting temperatures that generally fall between those of polyethylene and polypropylene.

The blends, obtained by co-precipitation from solution of the two components, contained 10–30 wt.% of LCP polyester.

The thermal stability of the blends was found to depend on the nature and composition of the polymeric components, and on the atmospheric conditions (air or nitrogen atmosphere).

When analysed under nitrogen atmosphere, the thermal stability of the blends was found to be intermediate between the more stable polyolefin and the less stable LCP. However, under air atmosphere, the thermal decomposition is mainly regulated by the thermal oxidation of the polyolefin, which decomposes at a lower temperature than the LCP component.

The same trend holds for blends of any analysed composition. From analysis of the DTG profiles, a dilution effect can be deduced as being responsible for the blend stability under nitrogen atmosphere. Under air atmosphere, no precise explanation can be suggested for the more complex thermal oxidation that is induced in the polyolefin component.

Any relevant effect resulting from the structural features of the LCP could be investigated by analysis of more LCP samples with variable lengths of flexible spacer.

As a general remark, it must be stressed that the thermal decomposition of the polyolefin–LCP blends is governed by the relevant characteristics of the less stable component, rather than by the miscibility of the two components in the blends.

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