

Thermogravimetric analysis of liquid crystal–polymer blends

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Abstract

Blends of semi-crystalline polymers, i.e. poly(ethylene adipate) (PEA) and polytetrahydrofuran (PTHF), with cholesteryl palmitate (CP) as a low molecular weight liquid crystal were characterized by thermogravimetric analysis under dynamic conditions. The resulting data, together with the analysis of activation energies, demonstrate that adding the low molecular weight component determines different thermal behaviour for these blends.

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1. Introduction

Low molecular weight liquid crystals in polymer matrices constitute interesting systems from many points of view. Many studies concerning phase behaviour, miscibility, morphology and properties have been done on such blends [1–5]. For example, Rodrigues et al. [1] studied the microscopic behaviour of blends of poly(ethylene oxide) with two different low molecular weight liquid crystals in order to evaluate miscibility and found that the melting temperature depression of polymer increased with liquid crystal content. This result suggests that the polymer is miscible with both liquid crystals in isotropic phase. Riccardi et al. presented in [2] a thermodynamic analysis of phase equilibrium in polydisperse polymer–liquid crystal blends. In this study three different systems were chosen: (1) a high molar mass polydisperse polystyrene blended with 7 CB as the low molecular weight liquid crystal; (2) a low molar mass

polydisperse polystyrene blended with 7 CB; (3) an epoxy-based thermosetting polymer blended with nematic mixture E 7. Also, these systems can be used in interesting applications [6–9]. For example Carpaneto et al. [8] investigated the phase separation behaviour of composite films made of E 7 embedded in a thermoplastic matrix of poly(butyl methacrylate) or poly(methyl methacrylate). The authors found that the two systems exhibit distinct mechanisms of phase separation. The poly(butyl methacrylate)–E 7 composites because of the low T_g of the polymer and the high solubility of the liquid crystal in the matrix at room temperature seem to be unsuitable for polymer-dispersed liquid crystal application, whereas a higher degree of phase separation was found for the poly(methyl methacrylate)-based films. Lin and Chien [9] synthesized main chain liquid crystal epoxies for the phase separation with E 7 and studied for their mesomorphic properties and response to an applied electric field.

Semi-crystalline polymers can be used as non-interactive supports for liquid crystals in these devices. Because of these applications, liquid crystal–polymer

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blends have attracted considerable attention in the microelectronics industry. In this case, however, an immiscible polymer–liquid crystal blend is advantageous because one is interested in preserving the birefringent behaviour of the liquid crystal impregnated in polymeric substrate.

In a previous paper [10] we characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy blends of poly(ethylene adipate) (PEA) ($M_n = 2000$ g/mol) and polytetrahydrofuran (PTHF) ($M_n = 1000$ and 2000 g/mol) with cholesteryl palmitate (CP) as a low molecular weight liquid crystal, and it was found that these blends present some concentration-dependent miscibility, and an improved miscibility was found for the blends with PEA, caused by the similar chemical structure and stronger interactions between the two components.

In this work, we continue our investigations on these blends using thermogravimetric analysis as a complementary method with the purpose of establishing the presence of interactions in these blends. The thermal behaviour studies were performed under dynamic conditions of temperature, by applying thermogravimetry (TG) and derivative thermogravimetry (DTG), using the same operational parameters in order to obtain comparable results.

2. Experimental

2.1. Materials

PEA with endcapped hydroxyl groups is a commercial product purchased from Fibrex SA, Savinesti, Romania ($M_n = 2000$ g/mol). PTHF with $M_n = 1000$ and 2000 g/mol are commercial products purchased from BASF. Cholesteryl palmitate CP was obtained from Nopris SRL, Cluj Napoca, Romania and used as received. This LC compound presents two types of mesophases, i.e. cholesteric and smectic mesophases: m.p. (C-Ch) 78 °C, (Ch-I) 81 °C, (Ch-S) 73 °C (monotropic) (as determined by DSC, 4 K/min). 1,2-Dichloroethane (DCE) (Aldrich) was used as received.

2.2. Blend preparation

The polymers and CP were separately dissolved in DCE to form 2 and 0.8 g/dl solutions, respectively.

Then, the solutions were mixed to the final ratio and the mixtures were stirred for 5 h. After that, the solvent was slowly evaporated at room temperature. In order to remove the residual solvent, the samples were dried in a vacuum oven at 50 °C for several days.

2.3. Measurements

The thermo-oxidative behaviour was studied on a MOM-Budapest derivatograph of the Paulik-Paulik-Erdey type (heating rate of 12 K/min, sample mass: 50 mg, air flow rate: 30 ml/min, aluminium oxide as reference, temperature domain: 20 – 600 °C).

3. Results and discussion

The thermogravimetric curves of PEA-based blends and PTHF 1000-based blends are plotted in Figs. 1 and 2, respectively. It can be noticed that the low molecular weight liquid crystal is less stable than PEA and more stable than PTHF. In the case of blends based on PEA, higher amounts of additive leads to an increase of the rate of mass loss, while in the PTHF-blends an opposite effect is obtained: the low molecular weight liquid crystal leads to a rise in thermal stability.

Based upon the mass loss curves of the pure components, theoretical curves (additive curves calculated as average value of each point on the TG curves of components that suppose no interaction between components to occur) were calculated and it was found that for some of the blends with PEA, the experimental

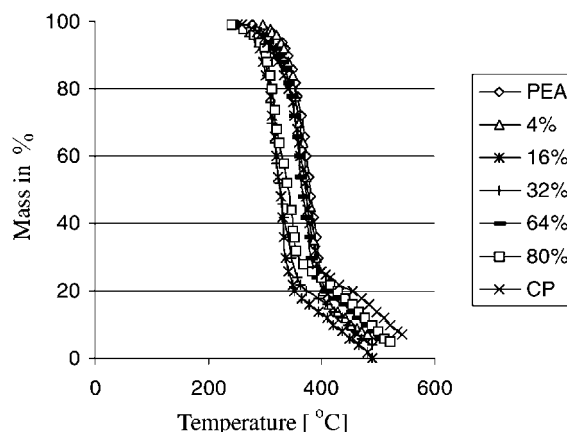


Fig. 1. Thermogravimetric curves of blends with PEA.

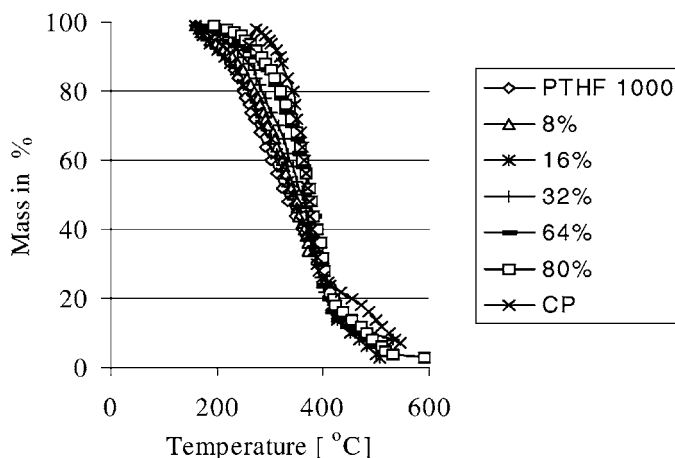


Fig. 2. Thermogravimetric curves of blends with PTHF 1000.

curves show higher rates of mass loss as compared with the theoretical ones (Fig. 3), proving the existence of degradation interactions [11] between the components. For the PTHF-based blends the experimental curves are almost superposed (Fig. 3) with the theoretical ones, caused by the weaker interactions involved in these blends.

The thermal characteristics obtained from TG and DTG curves are presented in Tables 1–3.

From Table 1 it can be noticed that, in general, in the thermo-oxidative decomposition, two consecutive stages can be distinguished: the main stage being followed by a final one. It can be mentioned here that

for aliphatic polyesters, as in the case of simple low molecular weight esters, the principal mode of thermal breakdown is ester decomposition via a cyclic transition state producing acid and olefin [13]. A different behaviour was obtained at the blend with 80% CP when three stages are seen. The second stage is characterized by a lower value of activation energy, suggesting a decrease in thermal stability. Also, the temperature corresponding to a 5% loss in mass ($T_{\alpha=0.05}$), regarded as a criterion of stability, shows that the additive causes a lower thermal stability.

From Table 2, where the thermal characteristics of the blends with PTHF 1000 are listed, it can be

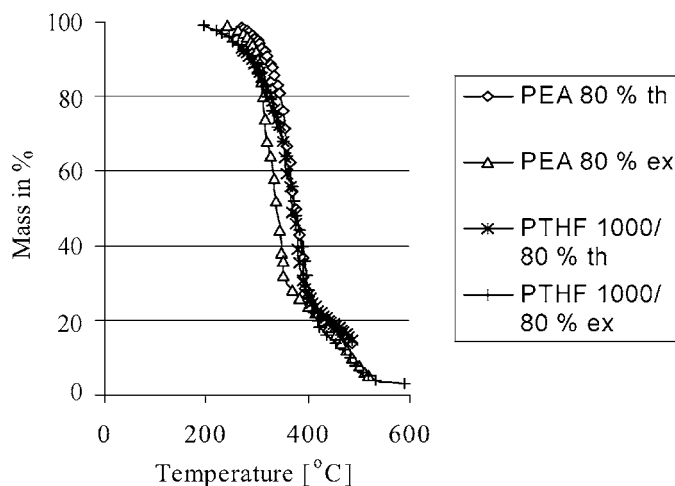


Fig. 3. The experimental and theoretical thermogravimetric curves of PEA-based blends and PTHF 1000-based blends with 80% CP.

Table 1
Thermal characteristics of PEA-based blends

| CP (%) | Stages | °C | T_{\max} (°C) ^a | Mass loss (%) | $T_{\alpha=0.05\text{ex}}$ ^b (°C) | $T_{\alpha=0.05\text{th}}$ (°C) | E_{CR} ^c (kJ/mol) | n^d |
|--------|--------|---------|------------------------------|---------------|--|---------------------------------|---------------------------------------|-------|
| 0 | I | 220–442 | 385 | 89 | 325 | 325 | 120 | 0.8 |
| | II | 442–510 | – | 7 | | | | |
| 4 | I | 235–435 | 385 | 87.5 | 325 | 322 | 160 | 1.3 |
| | II | 435–493 | – | 5.5 | | | | |
| 16 | I | 220–378 | 335 | 84 | 283 | 320 | 151 | 1.1 |
| | II | 378–518 | – | 16 | | | | |
| 32 | I | 200–388 | 325 | 81 | 288 | 312 | 135 | 1.0 |
| | II | 388–505 | – | 15 | | | | |
| 64 | I | 210–432 | 370 | 83 | 300 | 304 | 84 | 0.3 |
| | II | 342–520 | – | 12 | | | | |
| 80 | I | 210–332 | 320 | 42 | 288 | 302 | 82 | 0 |
| | II | 332–385 | 350 | 32 | | | | |
| | III | 400–532 | – | 21 | | | | |
| 100 | I | 245–415 | 370 | 76 | 300 | 300 | 96 | 0.6 |
| | II | 452–545 | – | 17 | | | | |

^a Temperature corresponding to the maximum rate of decomposition.

^b Temperature corresponding to a 5% loss in mass; ex: from experimental curves; th: from theoretical curves.

^c Activation energy as determined by Coats–Redfern method [12].

^d Order of decomposition reaction as determined by Coats–Redfern method.

observed that blending causes a decrease in the number of decomposition stages as compared with the parent PTHF and also the appearance of inflections on the DTG curves, suggesting that there are interactions between the two components. $T_{\alpha=0.05}$ increases with increasing content of the liquid crystal component, evidencing thermal stabilization.

As for the PTHF 2000-based blends, a pronounced effect of decreasing the number of decomposition stages and an increased number of inflections are observed. Concerning the $T_{\alpha=0.05}$ values, the same result is obtained, showing the increased thermal stability determined by CP.

It is known that, of all the kinetic parameters which could be used to characterize thermal stability, only the activation energy (E_a) could be considered as a semiquantitative factor [14,15]. Hence, in carrying out a comparative investigation on thermal decomposition of the studied products, the change of activation energy as a function of conversion was followed by using the Levi-Reich kinetic analysis method [16,17]. The values of reaction order employed in these calculations were estimated by means of the Coats–Redfern method. The activation energies and orders of

decomposition reactions for the thermo-oxidative degradation of the studied blends are presented in Tables 1–3 (E_{CR} and n).

For the blends with PEA the first stage of decomposition was chosen in the calculation of the above-mentioned parameters, while for the blends with PTHF the decomposition stages corresponding to a value of T_{\max} of about 400 °C were chosen.

One can observe that for the blends with PEA with higher content of CP, lower values of activation energies and orders of reaction are obtained, while for the blends with lower content of additive, higher values of activation energies and orders of reaction are seen. The dependence of activation energy on conversion for PEA blends is illustrated in Fig. 4. The E_a of CP, after the original sharp decrease caused by the loss of the light degradation compounds such as CO₂ [18], remains constant up to 50% conversion, after which it shows a slight rise as degradation proceeds, which means that the stability of the intermediate products are rather similar. The activation energy of PEA exhibits a rise even at low conversion, this fact evidencing that PEA is more stable than the additive. The behaviour of the blend with 4% CP is closer to that of

Table 2
Thermal characteristics of PTHF 1000-based blends

| CP (%) | Stages | °C | T_{max} (°C) | Mass loss (%) | $T_{d=0.05ex}$ (°C) | E_{CR} (kJ/mol) | n |
|--------|--------|---------|----------------|---------------|---------------------|-------------------|-----|
| 0 | I | 150–180 | i ^a | 3 | 190 | – | – |
| | II | 180–282 | 255 | 29 | | – | – |
| | III | 282–368 | 320 | 30 | | – | – |
| | IV | 368–450 | 415 | 25 | | 7 | 0.0 |
| | V | 450–525 | 490 | 8 | | – | – |
| 8 | I | 140–210 | 178 | 8 | 190 | – | – |
| | II | 210–305 | i | 26 | | – | – |
| | III | 330–440 | 385 | 58 | | 37 | 0.7 |
| | IV | 440–495 | 450 | 5 | | – | – |
| 16 | I | 145–210 | 180 | 9 | 180 | – | – |
| | II | 210–305 | 275 | 27 | | – | – |
| | III | 305–380 | 369 | 30 | | – | – |
| | IV | 380–450 | 408 | 24 | | 24 | 0.4 |
| | V | 450–512 | – | 7 | | – | – |
| 32 | I | 150–215 | 185 | 5 | 215 | – | – |
| | II | 215–320 | 310 | 27 | | – | – |
| | III | 330–378 | 368 | 29 | | – | – |
| | IV | 378–445 | 390 | 24 | | 9 | 0.0 |
| | V | 445–520 | – | 11 | | – | – |
| 64 | I | 150–212 | 180 | 3.5 | 235 | – | – |
| | II | 212–320 | i | 18.5 | | – | – |
| | III | 320–435 | 398 | 65 | | 42 | 0.1 |
| | IV | 435–528 | – | 9 | | – | – |
| 80 | I | 170–218 | i | 2 | 255 | – | – |
| | II | 218–320 | i | 18 | | – | – |
| | III | 320–450 | 398 | 65 | | 52 | 0.5 |
| | IV | 450–555 | – | 12 | | – | – |
| 100 | I | 245–415 | 370 | 76 | 300 | 96 | 0.6 |
| | II | 452–545 | – | 17 | | – | – |

^a i: inflection on the DTG curve.

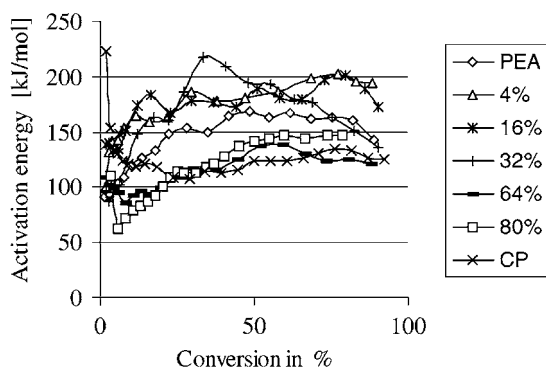


Fig. 4. Variation of activation energy as a function of conversion for PEA-based blends.

PEA but presents a higher value of activation energy. The E_a of the other blends after the decrease at low conversion exhibits an increase as degradation proceeds, higher values being obtained for the blends with 32 and 16% CP and lower values for the blends with 64 and 80% CP. These observations are in good agreement with the data obtained by the Coats–Redfern method.

Also, the theoretical curves representing the variation of E_a vs. conversion were calculated for these blends. It was found that the behaviour of experimental curves for the blends with 4 and 16% CP is closer to that of the theoretical ones but the former curves show higher values of energy. As for the blend with 32%

Table 3
Thermal characteristics of PTHF 2000-based blends

| CP (%) | Stages | °C | T_{\max} (°C) | Mass loss (%) | $T_{x=0.05ex}$ (°C) | E_{CR} (kJ/mol) | n |
|--------|--------|---------|-----------------|---------------|---------------------|-------------------|-----|
| 0 | I | 150–210 | i ^a | 5 | 210 | – | – |
| | II | 210–285 | 258 | 37 | | – | – |
| | III | 315–368 | 340 | 20 | | – | – |
| | IV | 368–442 | 402 | 24 | | 10 | 0.0 |
| | V | 442–515 | – | 9 | | – | – |
| 8 | I | 160–220 | 192 | 7 | 205 | – | – |
| | II | 220–325 | i | 29 | | – | – |
| | III | 325–450 | 400 | 54 | | 33 | 0.5 |
| | IV | 450–505 | 460 | 7 | | – | – |
| 16 | I | 170–202 | i | 4 | 210 | – | – |
| | II | 202–342 | 318 | 42 | | – | – |
| | III | 342–440 | 398 | 44 | | 28 | 0.4 |
| | IV | 440–510 | 470 | 5 | | – | – |
| 32 | I | 170–215 | 185 | 3 | 238 | – | – |
| | II | 215–325 | i | 22 | | – | – |
| | III | 325–435 | 402 | 63 | | 39 | 0.2 |
| | IV | 435–530 | 470 | 7 | | – | – |
| 64 | I | 170–220 | i | 2 | 262 | – | – |
| | II | 220–325 | i | 18 | | – | – |
| | III | 325–435 | 398 | 67 | | 53 | 0.4 |
| | IV | 435–535 | 478 | 9 | | – | – |
| 80 | I | 170–200 | i | 1.2 | 278 | – | – |
| | II | 225–325 | i | 14.8 | | – | – |
| | III | 325–435 | 400 | 70 | | 62 | 0.4 |
| | IV | 435–538 | 480 | 8 | | – | – |
| 100 | I | 245–415 | 370 | 76 | 300 | 96 | 0.6 |
| | II | 452–545 | – | 17 | | | |

^a i: inflection on the DTG curve.

additive, the experimental curve shows for the initial stage of decomposition lower values of activation energy than those corresponding to the theoretical curve, but as degradation proceeds the E_a of the experimental curve increases to higher values when it reaches a maximum, after which it decreases to values closer to those of the theoretical curve. The experimental curves of the blends with 64 and 80% CP show lower values of energy than the theoretical ones up to a 40% conversion, followed by a rise of E_a when the experimental values of activation energy are closer to those of theoretical curves. When a polymer blend is subjected to thermal degradation conditions, it is possible that the blends' constituents or their degradation products interact with each other, thus modifying the degradation behaviour with respect to that of the pure components. The results presented in this paper

evidence the existence of interactions in these blends and the thermal behaviour depends on the amount of the additive.

The plots of experimental and theoretical curves of the blends with 4 and 80% additive are portrayed in Fig. 5.

With respect to the PTHF-based blends, it is obvious that the E_{CR} values increase by adding the low molecular weight liquid crystal, evidencing the thermal stabilization caused by the latter. Plots of activation energy vs. conversion for these blends are represented in Fig. 6. As it can be noticed, initially an abrupt drop of activation energy is taking place, and subsequently it remains constant with increasing conversion. The conversion range corresponding to the constant E_a becomes broader as the amount of CP increases in the blend.

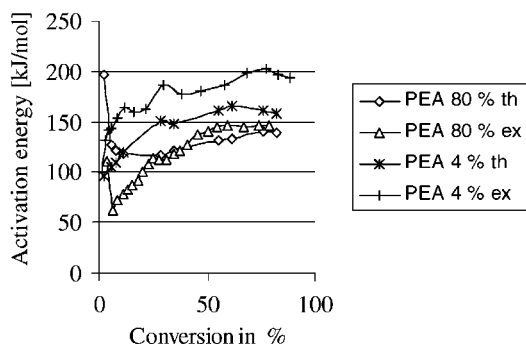


Fig. 5. The theoretical and experimental curves representing the dependence of activation energy vs. conversion for PEA-based blends with 4 and 80% CP.

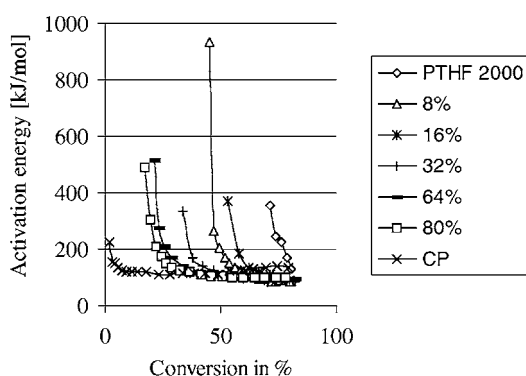


Fig. 6. Variation of activation energy as a function of conversion for PTHF 2000-based blends.

4. Conclusions

Adding the low molecular weight liquid crystal to these polymers causes a different thermal behaviour. The blends with polyester (PEA) at lower amounts of additive show higher values of activation energy, while higher amounts of additive caused an opposite effect. The blends with polyether (PTHF) are characterized by a thermal stabilization in the presence of the additive. The shifts of experimental thermogravimetric curves as compared with the theoretical thermogravimetric curves demonstrate the existence of the degradation interactions in the blends with polyester. A different result was obtained in the case of polyether blends, which show a superposition of these curves.

As it has been already mentioned, these blends were studied previously by DSC and polarizing optical microscopy and it was found that these blends present

some concentration-dependent miscibility, and an improved miscibility was found for the blends with polyester, caused by the similar chemical structure and stronger interactions between the two components. Miscibility studies and implicitly the studies of interactions between the blends' constituents are important for these systems since when applying, non-interactive polymeric supports are desired.

In this paper thermogravimetric analysis was employed as a complementary method in order to put into evidence the presence of interactions in these blends. The results of the present investigation prove the existence of these interactions and offer a more complete image concerning the characterization of these blends.

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