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Heating rate effect on char yield from cotton, poly(ethylene terephthalate) and blend fabrics

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ABSTRACT

Thermal behaviour of polymers is generally assessed by relatively low heating rate, such as in thermogravimetry (typically at 10 °C/min), which leads to progressive decomposition of chemical bonds with increasing dissociation energy under thermodynamic control. However, polymer materials may be accidentally exposed to high heating rates such as in a fire, when their thermal decomposition, occurring through competing paths, becomes kinetically controlled and may lead to heating rate dependence of their degradation mechanisms and products. In the present paper, thermogravimetry at 100, 200 and 300 °C/min heating rates has been carried out on cotton, poly(ethylene terephthalate) and their blend fabrics, which decompose with partial charring. The obtained results show that the char, produced by thermal and thermo-oxidative degradation of such polymer materials, is affected by the heating rate essentially in terms of thermal stability and yield, depending on the type of polymer and the absence or presence of air oxygen.

1. Introduction

Thermogravimetry (TG) is the most widely used tool for studying the thermal and thermo-oxidative degradation of polymers. Indeed, it supplies quantitative results regarding weight loss of a sample and corresponding rate (dTG), as functions of temperature or heating time (in isothermal conditions), provided that thermal lag effects and temperature gradients across the sample are taken in account and properly corrected.

The thermal degradation of cotton (cellulose) (Abidi, Hequet, & Ethridge, 2007; Abidi et al., 2008; Antal & Varhegyi, 1995; Chatterjee & Conrad, 1966; Faroq, Price, & Milnes, 1994; Golova, 1975; Horrocks, 2001; Horrocks, Price, & Akalin, 1996; Kilzer & Broido, 1965; Low & Morterra, 1985; Morterra & Low, 1984, 1985a, 1985b; Morterra, Low, & Severdia, 1984; Price, Horrocks, Akalin, & Faroq, 1997; Shafizadeh, Newell, & Zeronian, 1985) and poly(ethylene terephthalate), PET (Botelho, Queiros, & Gijsman, 2001; Bounekhel & McNeill, 1995; Buxbaum, 1968; Holland & Hay, 2002; Khemani, 2000; Lecomte & Liggat, 2006; Levchik & Weil, 2004; McNeill & Bounekhel, 1991; Montaudo, Puglisi, & Samperi, 1991, 1993; Nait-Ali, Colin, & Bergeret, 2011; Romao et al., 2009; Samperi, Puglisi, Alicata, & Montaudo, 2004a, 2004b; Sebastianelli, Alongi, Battegazzore, & Camino, 2009; Yoda, Tsubol, Wada, & Yamada, 1970; Zimmerman & Kim, 1980) has been extensively studied by TG and TG coupled to analytical techniques, to identify the species released to gas phase (Levchik & Weil, 2004; Montaudo et al., 1991, 1993; Samperi et al., 2004a, 2004b) or left as a thermally stable residue (Holland & Hay, 2002), in order to establish cellulose and PET degradation mechanism in inert and oxidative atmospheres.

The thermal degradation of cellulose takes place at 300–400 °C through two competitive processes, namely depolymerisation (1) and dehydration (2), as schematised in Fig. 1. Depolymerisation is initiated by the scission of acetal bonds between the chain glycosidic units, followed by successive splitting of volatile laevoglucosan, the cyclic monomer of cellulose, from ensuing chain ends (Horrocks, 2001).

Competing dehydration reactions lead to thermally stable aliphatic structures (char I), which subsequently are converted into aromatic structures (char II), with water, methane, carbon mono and dioxide evolution (400–600 °C). Char II (ca. 18%) is thermally stable at least up to 800 °C.

On heating PET undergoes ester bond scission (route 1 in Fig. 2), for which a radical (Bounekhel & McNeill, 1995) or an ionic (Sebastianelli et al., 2009) mechanism has been proposed, producing carboxy- and vinyl-terminated chain fragments. These reactive end groups can either produce volatile cyclic oligomers by backbiting depolymerisation mechanism (route 2 in Fig. 2) or, being unstable at the scission temperature (400–500 °C), can further decompose with the formation of volatile moieties such as carbon mono- and dioxide, methane, ethylene, benzene, benzaldehyde, formaldehyde and acetaldehyde (Bounekhel & McNeill, 1995;

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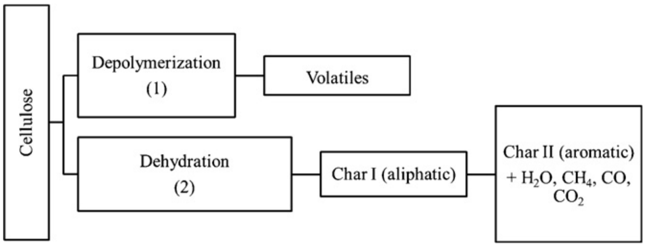

Fig. 1. Scheme of cotton degradation.

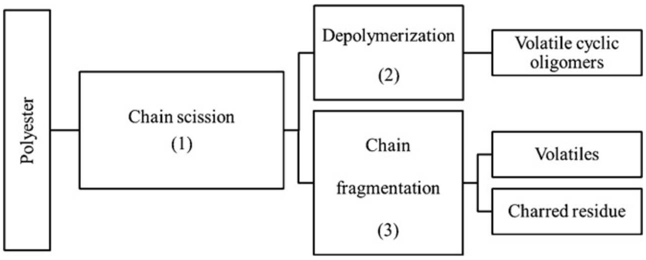

Fig. 2. Scheme of polyester degradation.

Khemani, 2000; McNeill & Bounekhel, 1991; Sebastianelli et al., 2009; Zimmerman & Kim, 1980). Progressive statistical chain fragmentation may produce chain fragments of low enough molecular weight to be volatile at the degradation temperature. The probability of chain fragment volatilisation increases with heating time, owing to PET progressive decrease of molecular weight. The interconnection of PET aromatic rings (route 3 in Fig. 2), promoted by reactive species produced either by the decomposition of chain end groups (Sebastianelli et al., 2009) or by ester-phthalic ring bond scission (Holland & Hay, 2002), has been proposed for justifying the thermal stabilisation of chain fragments issued by chain scission, with the production of about 10% charred residue stable at least up to 800 °C.

Indeed, in charring polymers such as cotton and PET, the yield and thermal stability of the char is relevant to their ignition and burning behaviour. As a matter of fact, the char has a tendency to cumulate onto the surface of the degrading material, thus controlling transfer of heat, oxygen and flammable volatiles between polymer and gas phase (Fina & Camino, 2011).

The above degradation mechanisms have been assessed by heating cellulose and PET either isothermally or at low heating rates (mostly at 10 °C/min), i.e. in conditions in which chemical bonds are progressively broken under thermodynamic control as functions of their thermal stability: thus, it has been possible to fully understand the close relationship between polymer chemical structure and thermal degradation process.

On the other hand, to the best of authors' knowledge, no literature data are available on cellulose and PET thermal and thermo-oxidative degradation under very fast heating rates, which are relevant for example when these polymers are exposed to a fire scenario. Before ignition, polymer thermo-oxidative degradation occurs at either low or very high heating rates depending on whether the polymer material initiates the fire or it is involved in a fully developed fire. Once the polymer is ignited, the oxygen diffusion through the flame is very limited and the polymer thermal degradation essentially occurs without oxygen involvement at high/very high heating rates due to flame irradiance essentially.

Cellulose and PET are one of the most used commercial textile polymers for furniture upholstery, which play a significant role in building fire propagation. Therefore, it is of paramount importance to know mechanisms and degradation products of such polymers in a very high heating rate scenario. For this reason, the present paper is focused to investigate the effect of 100, 200 and 300 °C/min heating rates on cotton, PET and a 65/35% PET/cotton blend.

2. Experimental

2.1. Materials

Cotton (COT, 210 g/m^2), polyester (PET, 170 g/m^2) and a PET–COT blend (65% PET, 245 g/m^2) fabrics were kindly supplied by Klopman International, Ltd. (Frosinone, Italy).

2.2. Characterisation techniques

TG was carried out in nitrogen or air, from 50 to 800 °C with a heating rate of 10, 100, 200 and 300 °C/min. To this aim, TAQ500 and TAQ5000IR thermobalances (experimental error: ±0.5 wt.%) were used, placing the samples (ca. 6 mg) in open platinum pans, in inert or oxidative atmosphere (gas flow: 60 and 25 ml/min). $T_{\text{onset}5\%}$ (temperature at which 5% weight loss occurs), $T_{\max}$ (maximum weight loss rate) and the mass of obtained residues were evaluated.

In order to overcome some limitations of TG analysis (i.e. thermal lag effects and temperature gradient across the sample) the mass of the tested samples was kept below 8 mg and, a single fabric piece was placed at the bottom of platinum pan, thus avoiding piling structures.

Hereafter, the samples will be coded as COT, PET or PET–COT combined with a number indicating TG heating rate.

2.3. Thermogravimetry kinetic theory

Thermogravimetry provides quantitative information regarding the weight loss (and the corresponding rate) of a sample, as a function of temperature or isothermal heating time.

The rate, at which a sample loses weight on heating, is defined as

$$\text{weight loss rate} = \frac{dc}{dt} \quad (1)$$

where

$$c = \frac{W_0 - W_i}{W_0} = 1 - \frac{W_i}{W_0} \quad (2)$$

In current TG kinetic discussions (Broido, 1969; Cameron & Rudin, 1981; MacCallum, 1979), it is assumed that the weight loss rate is a function of actual sample weight:

$$\frac{dc}{dt} = kf(c) \quad (3)$$

By unsupported formal analogy with chemical kinetics, the following form is usually selected for function *f*:

$$f(c) = (1 - c)^n \quad (4)$$

and the weight loss temperature dependence is attributed to the constant *k* through the typical Arrhenius-activated process relationship:

$$k = Ae^{-E/RT} \quad (5)$$

Thus, the rate expression for sample weight loss in TG becomes:

$$\frac{dc}{dt} = k(1 - c)^n = Ae^{-E/RT}(1 - c)^n \quad (6)$$

which can be used for interpolating TG experimental curves and supplies the three parameters (*A*, *E*, *n*) that allow predicting the material weight loss in any experimental condition. Obviously, there is no direct link whatsoever among *A*, *E* and *n* of Eq. (6) and their meaning in chemical kinetics (i.e. pre-exponential factor, activation energy and order of reaction of chemical degradation

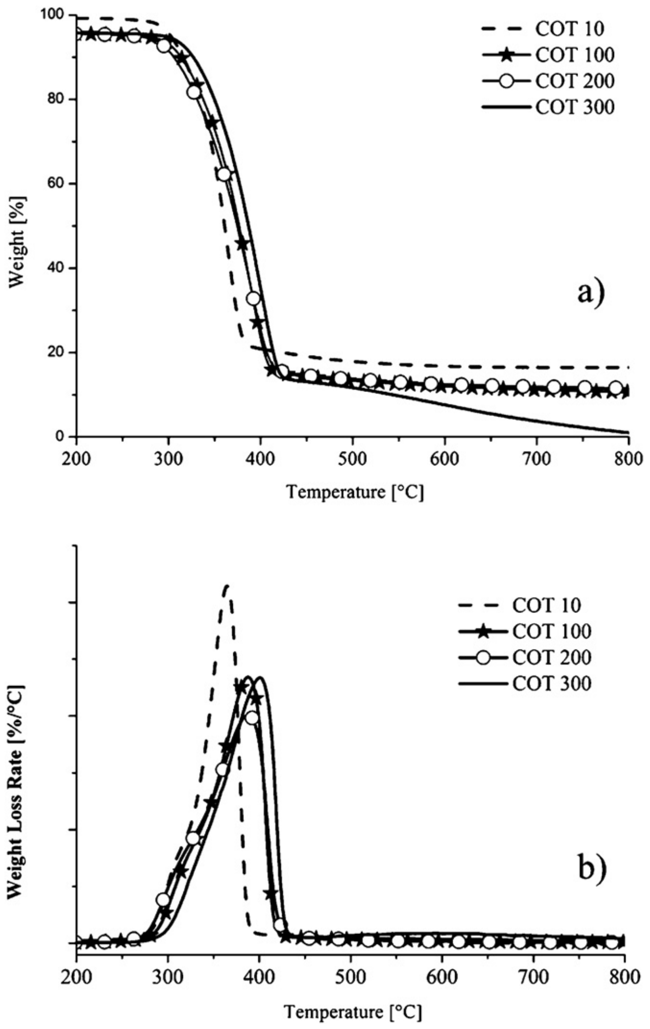

Fig. 3. TG (a) and dTG (b) curves of cotton in nitrogen.

reactions, respectively). Indeed, it can easily be shown (MacCallum, 1979) that, at the best, A and E are a complex combination of pre-exponential factor and activation energy of elementary reactions concurring to the production of volatile degradation species, while n turns out to be 1, irrespective of the complexity of the chemical reactions involved in degradation (Cameron & Rudin, 1981).

By including TG heating rate ($q = dT/dt$), Eq. (6) becomes:

$$\frac{dc}{dT} = \frac{A}{q} e^{-E/RT}(1-c)^{n} \qquad (7)$$

which shows that the weight loss rate is inversely proportional to heating rate, q (Broido, 1969).

3. Results and discussion

3.1. Char yield from cotton

TG and dTG curves of cotton heated in nitrogen at 10, 100, 200 and 300 °C/min are plotted in Fig. 3a and b, respectively; Table 1 summarises the collected data.

It can be seen that the degradation of cotton occurs at a higher temperature on increasing heating rate, as expected from Eq. (7). Indeed, at a given temperature, with increasing the heating rate (q), the degradation rate (dc/dT) decreases, so that the dTG curves of COT 100, COT 200 and COT 300 are shifted towards higher temperatures with respect to COT 10. Consequently, such samples exhibit higher temperatures of maximum weight loss with increasing heating rate (T_{max}, Table 1).

The charred residue yield of the main volatilisation process (350–400 °C) only slightly decreases from 21.5 to 16.0 with increasing the heating rate by one order of magnitude (from 10 to 100–300 °C/min). Since charring results from the dehydration process, it follows that its energy of activation is somewhat lower than that of competing depolymerisation reaction path (Fig. 1), as deduced from the activation energy effect on temperature dependence of chemical reactions. Indeed, by increasing the heating rate, the decomposition temperature increases which, in case of competition, favours reactions having high activation energy such as depolymerisation at the expenses of dehydration (Fig. 1).

In order to confirm such hypothesis, the well-known kinetic models reported in the literature (e.g. Ozawa, Friedman or Kissinger) could be used for calculating the activation energy as well as the pre-exponential factor. Indeed, in the literature, several papers exploit the Ozawa model (which is the most common) for determining the activation energy of pyrolysis of cellulose, as reported by Davies and Horrocks (1983) and Horrocks, Davies, and Greenhalgh (1985). Therefore, we have tried to calculate the activation energy by applying all the aforementioned models; however, they turned out to be not suitable for interpreting the degradation data obtained at very high heating rates (namely, 100, 200 and 300 °C/min). Indeed, these models usually are suitable for low heating rates (i.e. below 50 °C/min). To the best of our knowledge, no model describing the degradation kinetics at higher heating rates has been published so far. Indeed, the activation energies derived from the Ozawa model are always overestimated for all the conversion degrees. The only exception is represented by the lowest conversion degrees – i.e. 10 and 20% – for which the activation energies (ca. 140 kJ/mol) are in agreement with the data reported in the literature (range of 125–210 kJ/mol in Horrocks et al., 1985).

The char obtained by heating cellulose at 10–200 °C/min is essentially thermally stable to at least 800 °C (the highest temperature reached in the present work), whereas that produced by heating at 300 °C/min slowly undergoes degradation to volatiles above 500 °C reaching almost complete volatilisation at 800 °C. This finding can be ascribed to the higher thermal stability of the aromatic char II with respect to aliphatic anhydrocellulose char I (Fig. 1). At very high heating rates (>200 °C/min), aromatisation of anhydrocellulose may have not enough time to occur, thus slowly starting to decompose from 500 °C onwards.

In air, cotton degradation becomes more complex because of the presence of oxygen which, being a biradical, can chemically react with cellulose and/or its degradation products. Indeed, although the heating rate effect on the main volatilisation process (300–400 °C) takes place as in nitrogen (Fig. 4a and b) shifting the TG curves towards higher temperatures with increasing heating rate, the TG curves are shifted to ca. 10–20 °C lower temperatures with respect to nitrogen (compare Tables 1 and 2). This finding shows that oxygen chemically reacts with cellulose, initiating the volatilisation process at a lower temperature than by purely thermal initiation.

The residue yield at the end of the volatilisation step obtained at 10 °C/min in air (ca. 32%, Table 2) is much higher than in nitrogen (ca. 22%, Table 1). This might be ascribed to the charring increase due to oxidative dehydrogenation of anhydrocellulose, which leads to progressively more stable structures, thus shifting charring-depolymerisation competition in favour of charring. However, a heterogeneous structure is apparent for the residue obtained in air because half of it is slowly thermally degraded or oxidised between 350 and 450 °C, before undergoing fast complete oxidation to volatiles between 475 and 500 °C (T_{max2} = 502 °C, Fig. 4a and b, Table 2). The two char degradation steps may be due to mixed aliphatic (less stable) and aromatic (more stable) structures

Table 1
Thermogravimetric data of cotton in nitrogen.

Sample	$T_{onset5\%}$ (°C)	T_{max} (°C)	Residue at the end of volatilisation (%)	Residue at 800 °C (%)
COT 10	302	365	21.5	16.0
COT 100	308	390	19.0	13.7
COT 200	296	393	19.0	13.7
COT 300	293	401	16.0	1.0

Table 2
Thermogravimetric data of cotton in air.

Sample	$T_{onset5\%}$ (°C)	T_{max1} (°C)	Residue at the end of volatilisation (%)	T_{max2} (°C)
COT 10	280	344	32.0	502
COT 100	281	360	24.7	491
COT 200	282	362	17.4	491
COT 300	284	380	13.3	485

produced by anhydrocellulose charring in air, when thermal and thermo-oxidative processes simultaneously occur. Thus, the additional char produced in air by oxidative dehydrogenation might be essentially aliphatic, whereas thermally produced char is aromatic.

By increasing the heating rate, starting from 200 °C/min, a progressive decrease of char yield down to the value obtained in nitrogen is observed. This is due to the fact that the reaction between oxygen of air and degrading cellulose, which favours charring, is a heterophasic reaction, hence kinetically controlled by oxygen diffusion in the condensed phase. If the heating rate is too high (≥200 °C/min), oxidative dehydrogenation does not have enough time to take place, the degradation process becomes purely thermal and the features of thermal behaviour in nitrogen are resumed.

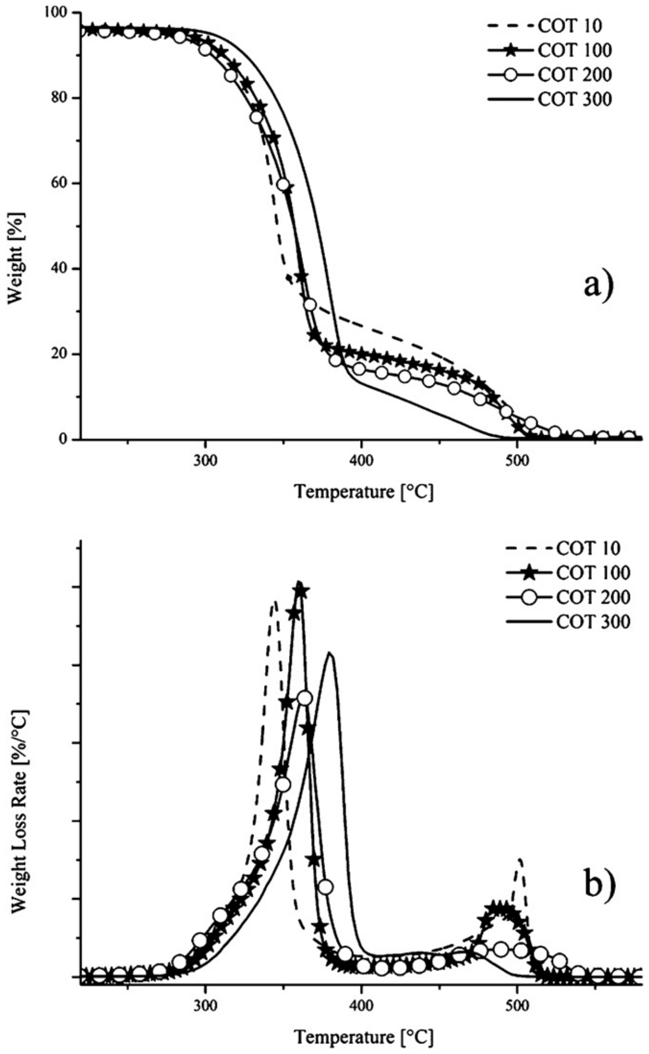

Fig. 4. TG (a) and dTG (b) curves of cotton in air.

The char obtained on heating at 300 °C/min, which should be comparable to that obtained in nitrogen, is completely volatilised by oxidation between 370 and 480 °C (Fig. 4a and b, Table 2), that is in the range of aliphatic char oxidation, in agreement with the wholly aliphatic structure of char suggested above and obtained under purely thermal control at this heating rate (Fig. 3a and b).

3.2. *Char yield from PET*

On heating at 10 °C/min, PET thermal degradation in nitrogen occurs through competing volatilisation-charring processes (Fig. 2) as in the case of cotton, but in a temperature range ca. 100 °C higher (420–500 °C, Fig. 5a and b, Table 3). Indeed, as expected from Eq. (7) and found in the case of cotton, TG curves are shifted to higher temperatures on increasing heating rates. At variance with cotton, PET decomposes with char yield (ca. 16%) almost independent of the heating rate, slightly decreasing to ca. 12% only at the highest heating rate (300 °C/min, Table 3). This datum makes clear that the competing formation of the volatiles and char from chain fragments are characterised by comparable activation energies.

On the contrary, the char stability is strongly affected by PET heating rate: indeed, at 10 °C/min, a char stable up to 800 °C as in the case of cotton is observed, whereas those obtained at high heating rates (i.e. 100, 200 and 300 °C/min) form volatile and products above 600 °C with a maximum rate between 660 and 690 °C (Fig. 5a and b, Table 3). The thermal stability of PET char does not show a simple relationship with the heating rate at which it is obtained, as shown by the crossover of char weight loss curves in Fig. 5a inlet. This is likely due to temperature dependent competition between different charring mechanisms, as those proposed in already mentioned references (Holland & Hay, 2002; Sebastianelli et al., 2009).

Oxygen in air has a negligible effect on the main volatilisation step of PET, occurring in a similar temperature range as in nitrogen (400–500 °C, Fig. 6a and b, Table 4). However, a complex effect, due to the presence of oxygen, is evident on yield and thermal stability of the char. Indeed, at low heating rates (10 °C/min), the char yield is slightly higher than that observed in nitrogen (ca. 20 vs. 16%, Tables 3 and 4) and is oxidised to volatile products with maximum rate at 557 °C. This result shows that the presence of

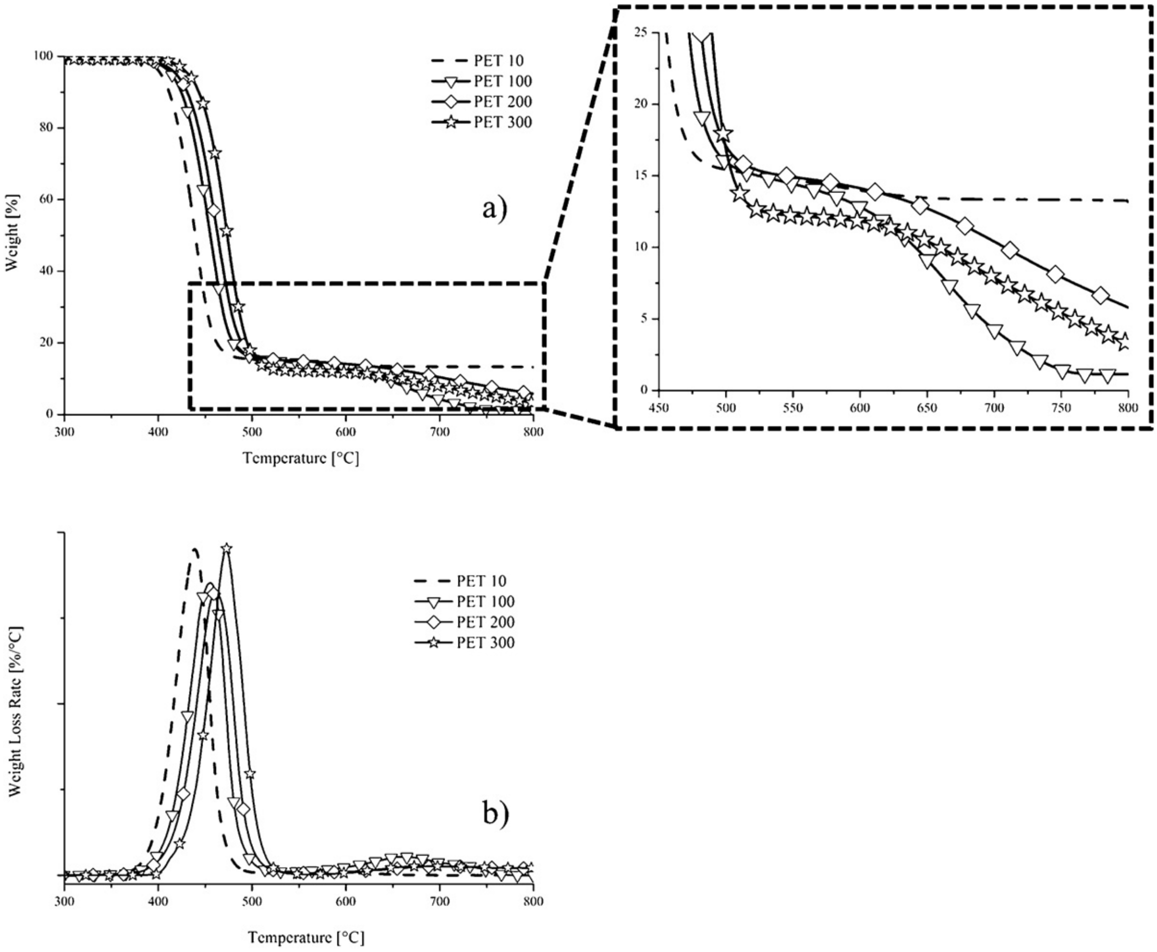

Fig. 5. TG (a) and dTG (b) curves of polyester in nitrogen.

oxygen do not affect the char formation at low heating rates, and thus the polyester degradation proceeds through the chain scission and fragmentation (routes 1 and 3, Fig. 2) giving rise to a stable residue. On the contrary, at 100–300 °C/min, the char yield in air is lower than that found in nitrogen; in addition, its stability is higher than that observed at 10 °C/min, since PET degradation proceeds preferably thorough depolymerisation by producing volatile species instead of char.

3.3. *Char yield from PET/cotton blend*

As previously assessed (Alongi, Carosio, & Malucelli, 2012a, 2012b; Carosio, Alongi, & Malucelli, 2012), at low heating rate (e.g. 10 °C/min) the thermal degradation of polyester–cotton blends in nitrogen shows an additive behaviour without any mechanistic interference between the two degrading polymers. Comparing the TG curves of Fig. 7a and b with the data collected in Table 5, it is

Table 3
Thermogravimetric data of PET in nitrogen.

Sample	$T_{onset5\%}$ (°C)	T_{max1} (°C)	Residue at end of volatilisation (%)	T_{max2} (°C)	Residue at 800 °C (%)
PET 10	403	439	15.8	–	13.3
PET 100	414	453	15.4	662	1.1
PET 200	420	461	15.2	693	5.8
PET 300	422	473	12.4	670	4.0

Table 4
Thermogravimetric data of PET in air.

Sample	$T_{onset5\%}$ (°C)	T_{max1} (°C)	Residue at end of volatilisation (%)	T_{max2} (°C)
PET 10	390	433	19.7	557
PET 100	412	451	13.3	602
PET 200	413	454	13.2	615
PET 300	427	466	11.4	594/626

Table 5
Thermogravimetric data of polyester–cotton blend in nitrogen.

Sample	$T_{onset5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Residue at end of volatilisation (%)	Residue at 800 °C (%)
PET–COT 10	332	365	433	15.9	11.2
PET–COT 100	332	380	453	15.7	1.0
PET–COT 200	333	381	458	15.4	3.0
PET–COT 300	340	403	471	13.4	6.0

clear that the almost same behaviour is found for 65/35 PET/cotton blend also at high heating rates. Thus, the main range of thermal volatilisation temperatures encompasses that of the two polymers (300–500 °C) and is characterised by two partially overlapping steps with a maximum rate between 365–403 °C and 433–471 °C, respectively, corresponding to the thermal volatilisation of cotton and PET. It is noticeable that the cotton volatilisation rate decreases with increasing heating rate, whereas that of PET is heating rate independent (Fig. 7b).

The char mixture produced by decomposition of the two polymers of the blend also shows an additive behaviour both in yield and thermal decomposition, with PET features dominating owing to its higher content in the fabric blend. In particular, the char obtained at 10 °C/min is thermally stable up to 800 °C, as in the case of pure cotton or PET thermal degradation, whereas those obtained at 100–300 °C/min start to decompose above 600 °C. However, at variance with chars obtained from neat PET degradation, those obtained on heating the blend show a regular increase of thermal stability by increasing heating rate from 100 to 300 °C/min.

The different behaviour of the blend can be attributable to the concurrent thermal degradation reactions of the two constituents: in particular, the char production from cotton fibres seems to affect the thermal degradation of PET, limiting the volatile production and favouring the char formation. As a consequence, the TG curves of the blend show a more regular trend than those of PET.

Also in air, the general TG trend of the blend, compared to that of neat cotton and PET, is substantially additive (Fig. 8a and b, Table 6), despite a larger increase of char yield at high heating rate, as compared to what is predictable on the basis of PET and cotton behaviour, separately, at the same conditions. The char yield of the blend is indeed the same as that obtained in nitrogen.

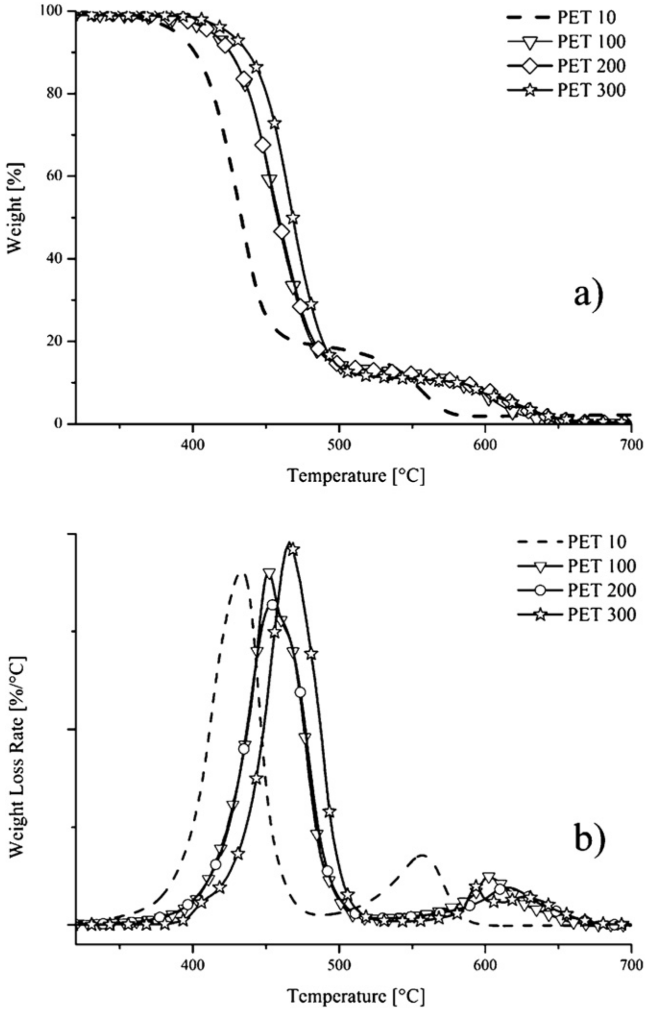

Fig. 6. TG (a) and dTG (b) curves of polyester in air.

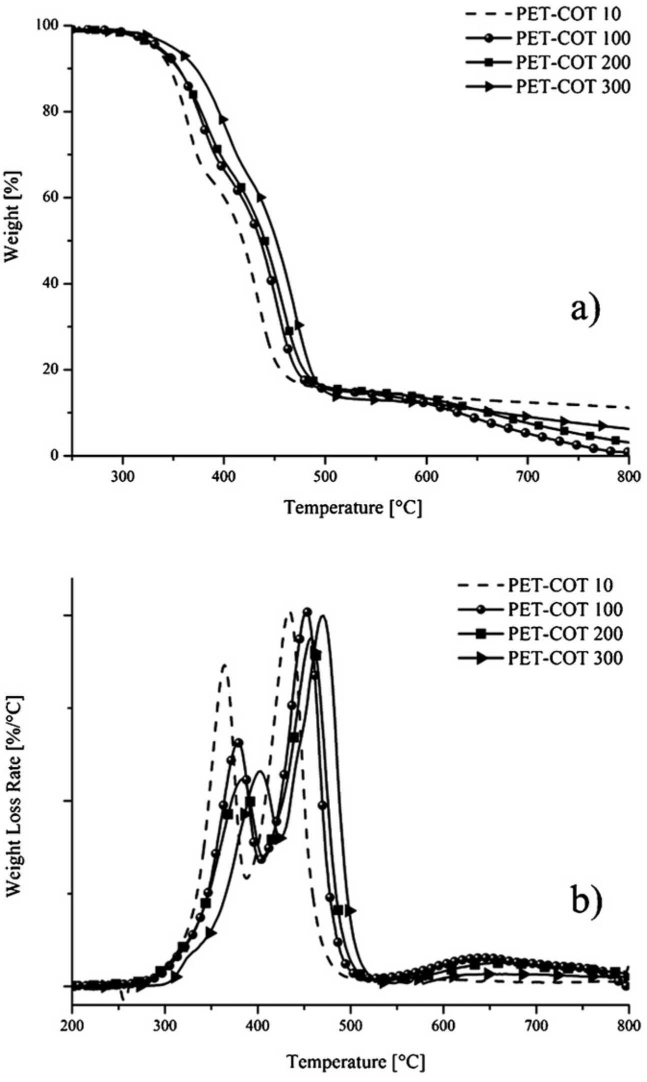

Fig. 7. TG (a) and dTG (b) curves of polyester–cotton blend in nitrogen.

Table 6
Thermogravimetric data of polyester–cotton blend in air.

Sample	$T_{onset5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Residue at end of volatilisation (%)	T_{max3} (°C)
PET–COT 10	323	351	428	15.9	518
PET–COT 100	332	372	451	15.2	554
PET–COT 200	331	378	452	14.4	574
PET–COT 300	344	397	462	13.9	557/624

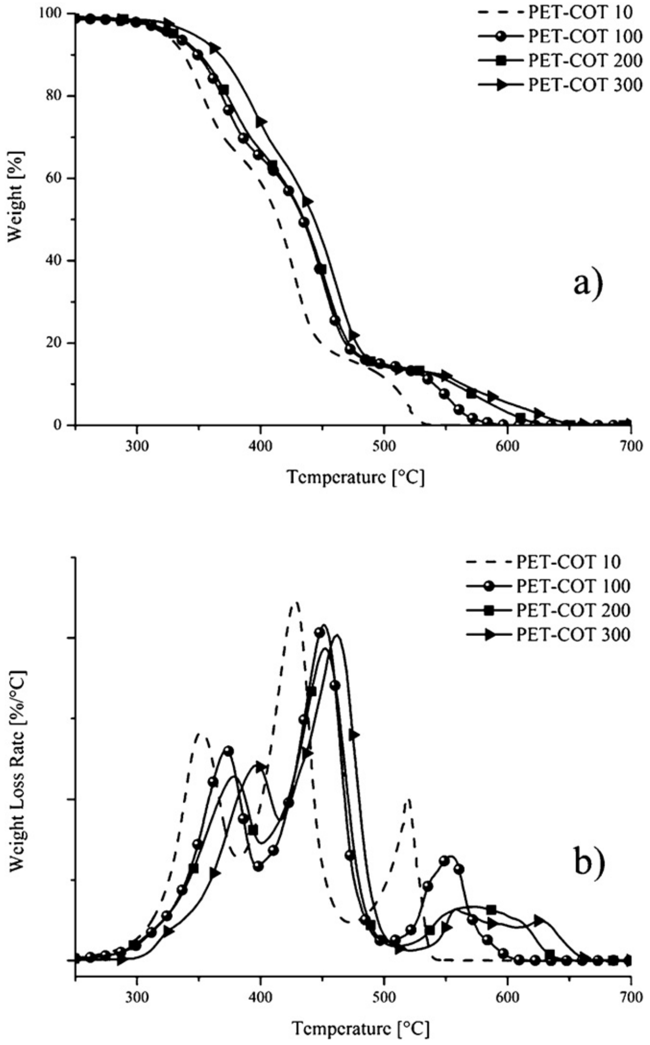

Fig. 8. TG (a) and dTG (b) curves of polyester–cotton blend in air.

4. Conclusions

Also at very high heating rates (100–300 °C/min), the overall degradation process of cotton and PET is the result of several competing reactions, which determine the yield of volatiles and the yield and thermal stability of the final char. In particular, the char produced by cotton and PET degradation in nitrogen at 10 °C/min is thermally stable up to 800 °C while, at very high heating rates, it decomposes at much lower temperatures.

When the degradation occurs in the presence of air oxygen, a further heating rate effect is found, depending on oxygen sensitivity of the chemical reactions of degradation occurring in the polymer condensed phase, in which oxygen diffusion is heating rate dependent. As an example, cotton and PET heated at low heating rate in air give a larger char yield than at high heating rates with variable thermal stability.

In the case of PET/cotton blends, at any heating rate used in this work, either in nitrogen or in air, the char production from cotton fibres seems to affect the thermal degradation of PET, limiting the volatile production and favouring the char formation.

Thus, thermal analyses carried out at variable heating conditions including very high heating rates are very important to characterise the thermal behaviour of polymers as well as to model and mimic the behaviour of polymers in the various thermal scenarios of fire stages.

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