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# Effect of compatibilization on thermal degradation kinetics of HDPE-based composites containing cellulose reinforcements

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**Abstract** Dynamic thermogravimetric analysis under nitrogen flow was used to investigate the thermal decomposition process of high-density poly(ethylene) (HDPE)-based composites reinforced with cellulose fibers obtained from the recycling of multilayer carton scraps, as a function of the cellulose content and the compatibilization. The Friedman, Flynn–Wall–Ozawa, and Coats–Redfern methods were used to determine the apparent activation energy ($E_a$) of the thermal degradation of the cellulose component into the composites. $E_a$ has been found dependent on the cellulose amount and on the cellulose/polymer matrix interfacial adhesion. In particular, it has been evidenced an increase of the cellulose thermal stability as a consequence of the improved interfacial adhesion between the components in NFR composites.

**Keywords** NFR composites · Cellulose · Compatibilization · TGA · Thermal degradation

## Introduction

Composites based on polymers filled with natural fibers, also called ecocomposites [1], have attracted the even growing attention from both scientific and industrial point of view [2–5]. Among several classes of polymeric matrices, polyolefins are the most used to realize natural fiber reinforced (NFR) composites. Unless virgin cellulose fibers are mainly used as reinforcement in composites, in the last years recycled cellulose has been also proposed, in many cases with very promising results, with the aim of contributing to the serious waste management problem [6, 7].

As an example, multilayer cartons (MC), mainly constituted by cellulose and low-density polyethylene (LDPE), are among the most used materials for food and beverage packaging applications, thus becoming the major constituent of the plastic waste stream.

The recyclability of such materials is a difficult task due to the concomitant presence of thermoplastic and cellulose components, and it needs the separation of single fractions [8]. Recently, an alternative mechanical recycling of MC has been proposed, based on the concept that these materials can be wholly reused as a source of cellulose fibers for the realization of polyolefin-based composites [9].

In NFR composites different surface properties between fibers and polyolefin matrices strictly require the set up of proper compatibilization strategies in order to improve the interfacial adhesion between components. For this purpose chemical modification of fibers or addition of a proper coupling agent are among the most effective approaches [10]. In particular, the addition of a coupling agent constituted by a polyolefin grafted with maleic anhydride is a widely used compatibilization strategy [11–14].

Due to the scientific and industrial relevance of this subject, many articles have been recently focused on the effect of cellulose reinforcements and cellulose/matrix compatibilization on the kinetic parameters of the thermal degradation of NFR composites. In particular, Kim et al. [15] report results on the activation energy of the thermal decomposition of poly(propylene) (PP)- and high-density poly(ethylene) (HDPE)-based composites reinforced with rice hulls. They hypothesize that compatibilization could have an influence on the kinetic parameters of thermal

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decomposition, unless their work is not focused on compatibilized systems. Bajer et al. [16] discuss results obtained on LDPE-based composites reinforced with waste paper concluding that the thermal stability of composites decreases by increasing the paper waste content. Nevertheless they evaluate the material thermal stability only in terms of maximum degradation rate, without dealing with kinetic parameters. Beg and Pickering [17] study the thermal stability of unbleached and bleached Kraft wood fiber reinforced PP composites. They report that compatibilization improves the thermal stability of composites. Nevertheless, in this case the compatibilization strategy, based on the chemical modification of cellulose, induces a significant increase of the activation energy for the thermal decomposition of modified cellulose itself, thus preventing a clear comprehension of the effect of compatibilization on the composite thermal stability.

Therefore it can be affirmed that, unless the research is currently focused on the set up of efficient compatibilization strategies between the phases constituting NFR composites, there is a lack of data concerning the possible protective effect of a polymer matrix onto the cellulose reinforcement, in particular in case of compatibilized composites.

On the basis of such a lack of information, the objective of this article was to investigate the influence of cellulose content and fibers/matrix compatibilization on the thermal decomposition process of cellulose fibers in HDPE-based composites. With this aim, the thermal stability and the apparent activation energy ($E_a$) of the thermal decomposition process were evaluated through thermogravimetric analysis, as well as the pre-exponential factor ($A$). In particular, $E_a$ values were calculated by applying three model-free methods to dynamic thermogravimetric data collected on compatibilized and uncompatibilized materials [18–20].

## Experimental

### Materials

Multilayer cartons, constituted by cellulose and LDPE (80/20 by mass), were kindly supplied by Tetra Pak Italiana S.r.l. (Latina, Italy), as production scraps. Scraps were milled in a Retsch SM100 cutting mill equipped with a bottom sieve (conidur holes, 1 mm diameter). The obtained powder was dried under vacuum at 90 °C overnight and kept in a desiccator.

High-density polyethylene (Alathon M6580, density 0.965 g cm$^{-3}$, melt index 8.2 g/10 min at 190 °C and 2.16 kg) was supplied by Equistar (Texas, USA).

Maleated linear LDPE, MAPE, trade name AGRIMAL-HD, density 0.92 g cm$^{-3}$, was kindly supplied by Agricola Imballaggi (Pagani, Italy). The content of maleic anhydride grafted onto polyethylene is 1% by mass, evaluated by titration [21].

### Composites preparation

HDPE/MC composites were compounded in an internal mixer (Rheocord EC of HAAKE Inc. New Jersey, USA). For uncompatibilized composites, HDPE was mixed with 40 and 60 mass/% of dried MC powder at 175 °C for 10 min. For compatibilized composites, HDPE was blended with 10 mass/% of MAPE at 175 °C for 10 min; then the blend was cooled and pelletized. Afterward, these pellets were mixed with 40 and 60 mass/% of dried MC powder at 175 °C for 10 min. Composites and neat HDPE were finally compression-molded at 180 °C in order to obtain 3.5 mm thick sheets. In Table 1, composition and codes of prepared materials are reported.

### Thermogravimetric analysis and data processing

Thermal decomposition processes were studied in terms of global mass loss by using a Perkin Elmer Pyris Diamond TG/DT analyzer. Samples were dried at 90 °C under vacuum for at least 48 h before testing. Therefore, they were placed in platinum open sample pans (capacity 90 μL) with an initial sample amount of $9 \div 10$ mg. The temperature program was set from room temperature (25 ± 3 °C) up to 800 °C at five different heating rates (2, 5, 10, 15, and 20 °C min$^{-1}$). The sampling was set as 1 point s$^{-1}$. High purity nitrogen stream (>99.99% nitrogen) was continuously fluxed into the furnace at a normalized flow rate of 50 mL min$^{-1}$.

In a first instance, mass loss (TG) curves obtained from TGA runs were used without further data processing. Therefore, as detailed in the further sections, in order to evaluate the conversion degree values of the thermal decomposition process of the cellulose component, the mass loss curves were normalized with respect to the real cellulose content. Mass loss rate (DTG) curves were carefully smoothed by adjacent averaging (number of adjacent points = 10). For linear regressions, standard

**Table 1** Composition and codes of prepared materials

| HDPE + MAPE (mass/%) | MC (mass/%) | MAPE/HDPE (mass ratio/%) | Codes |
|---|---|---|---|
| 100 | 0 | 0 | HDPE |
| 0 | 100 | 0 | MC |
| 60 | 40 | 0 | HDPE/MC 60/40 |
| 40 | 60 | 0 | HDPE/MC 40/60 |
| 60 | 40 | 10 | (HDPE + MAPE)/MC 60/40 |
| 40 | 60 | 10 | (HDPE + MAPE)/MC 40-60 |

deviation values were calculated using the software Microcal™ Origin™ 5.0 (Microcal Software, Inc., Northampton USA), whereas coefficient of determination values ($r^2$) were calculated as the square of the Pearson product-moment correlation coefficient ($r$) [22].

## Theoretical background

The fundamental equation applied in all kinetic studies is generally described as:

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \quad (1)$$

where $k$ is the rate constant, $f(\alpha)$ is a function depending on the reaction mechanism, and $\alpha$ is the conversion degree. For a species whose relative amount decrease during a reactive process the conversion degree $\alpha$ is defined as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\mathrm{f}} \quad (2)$$

where $W_0$, $W_t$, and $W_\mathrm{f}$ are initial, time $t$, and final mass of the sample, respectively. The rate constant $k$ is generally given by the Arrhenius equation:

$$k = A\ \exp(-E_\mathrm{a}/RT) \quad (3)$$

where $E_\mathrm{a}$ is the apparent activation energy (J mol$^{-1}$), $R$ is the gas constant, $A$ is the pre-exponential factor (min$^{-1}$), and $T$ is the absolute temperature (K). The combination of Eqs. 1 and 3 gives the following relationship:

$$\mathrm{d}\alpha/\mathrm{d}t = Af(\alpha)\exp(-E_\mathrm{a}/RT) \quad (4)$$

For a dynamic thermogravimetric process, the heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, should be considered. In this case Eq. 4 should be written as:

$$\mathrm{d}\alpha/\mathrm{d}t = (A/\beta)f(\alpha)\exp(-E_\mathrm{a}/RT) \quad (5)$$

Among the several available “model free” methods used to calculate the activation energy of the thermal decomposition process, in this study the Friedman, Flynn–Wall–Ozawa, and modified Coats–Redfern methods were applied. The Friedman method [18] is an isoconversional method based on the equation:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln[Af(\alpha)] - E_\mathrm{a}/RT \quad (6)$$

It directly leads to ($-E_\mathrm{a}/R$) for a given value of $\alpha$ by plotting the term $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ versus $1/T$ at any certain conversion rate.

The Flynn–Wall–Ozawa method [19, 23, 24] is another isoconversional method, based on the following equation:

$$\log\ \beta = \log\left[\frac{AE_\mathrm{a}}{Rf(\alpha)}\right] - 2.315 - \frac{0.4567\ E_\mathrm{a}}{RT} \quad (7)$$

From this integral method, $E_\mathrm{a}/R$ is obtained from the slope of $\log\ \beta$ versus $1/T$ at any certain conversion rate.

The modified Coats–Redfern method [20, 25] is a multi-heating rate application of the Coats–Redfern equation:

$$\ln\left[\frac{\beta}{T^2(1-2RT/E_\mathrm{a})}\right] = \ln\left[-\frac{AR}{E_\mathrm{a}\ln(1-\alpha)}\right] - \frac{E_\mathrm{a}}{RT} \quad (8)$$

From this method, $E_\mathrm{a}/R$ is calculated by an iterative method: in the first step $E_\mathrm{a}/R$ is obtained from the slope of $\ln[\beta/T^2]$ versus $1/T$: the obtained result is reported in the left term of Eq. 8 and the slope is recalculated by plotting the left term versus $1/T$. This process is carried out until convergence of $E_\mathrm{a}$ value. Finally, the pre-exponential factor, $A$, is obtained.

## Results and discussion

### Overall thermochemical decomposition processes

Figure 1 shows TG and DTG curves of HDPE and MC recorded at a heating rate of 20 °C min$^{-1}$. HDPE exhibits a single mass loss process, referred to the random chain scission occurring through a radical mechanism. The corresponding maximum mass loss rate ($T_\mathrm{max}$) has been found at 498 °C. As concerning MC, it shows three mass loss steps. The first one is a complex process including the decomposition of hemicellulose and cellulose, starting at 264 °C (evaluated at 1% mass loss) [26–28]. As expected, the associated DTG peak derives from the overlapping of the hemicellulose decomposition, whose process starts at lower temperature, and the α-cellulose decomposition,

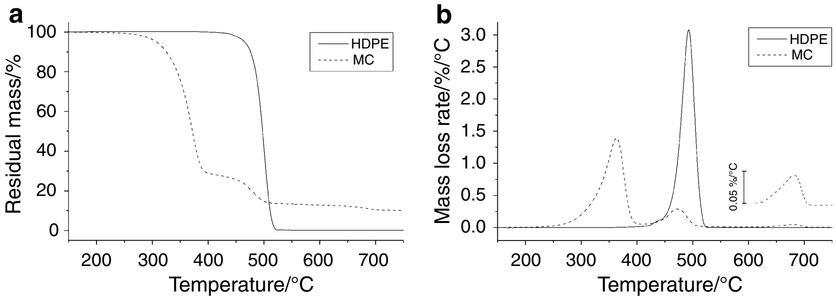

**Fig. 1** Overall thermochemical decomposition process of HDPE and MC at a heating rate of 20 °C min$^{-1}$: **a** residual mass (TG) traces; **b** mass loss rate (DTG) traces

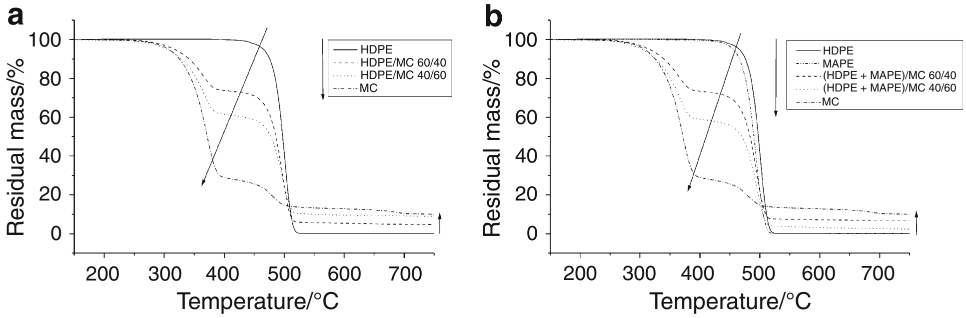

**Fig. 2** Overall thermochemical decomposition process of HDPE, MC, MAPE, and HDPE/MC composites at 20 °C min$^{-1}$ heating rate: **a** uncompatibilized composites; **b** compatibilized composites

occurring at higher temperature. Corresponding $T_{\max}$ for this multiple process has been found at 369 °C. This hemicellulose/cellulose decomposition only partially overlaps with the LDPE decomposition process, whose $T_{\max}$ has been recorded at 480 °C. Finally, the char degradation occurs at very higher temperature values, whose corresponding $T_{\max}$ is located at about 680 °C.

Figure 2 shows TG traces of uncompatibilized (Fig. 2a) and compatibilized (Fig. 2b) composites in comparison with HDPE, MC, and MAPE (coupling agent), recorded at 20 °C min$^{-1}$ heating rate. In particular, MAPE shows a reduced thermal stability with respect to neat HDPE. In fact, the onset for the thermal degradation process (evaluated at 1% mass loss and at heating rate of 20 °C min$^{-1}$) has been found 442 and 425 °C for neat HDPE and MAPE, respectively. Moreover, TG traces of both compatibilized and uncompatibilized composites lay between TG traces of neat HDPE and MC. A similar result has been reported by Kim et al. [15] on polyolefin-based composites reinforced with rice hull, as an evidence that the effect of a cellulose reinforcement is the improved thermal stability of the composites in comparison with the neat reinforcement. Nevertheless, such a kind of result can be differently explained by comparing the experimental TG curves for composites with theoretical curves obtained from the weighted average of neat HDPE and MC [29]. Very small differences have been found between theoretical and real curves, thus indicating that the improved thermal stability of the composites with respect to the neat reinforcement is only an illusory phenomenon. In fact, the improved thermal stability is a consequence of the mass ratio, within the composite, between the more thermally stable component (HDPE) with the less stable cellulose reinforcement.

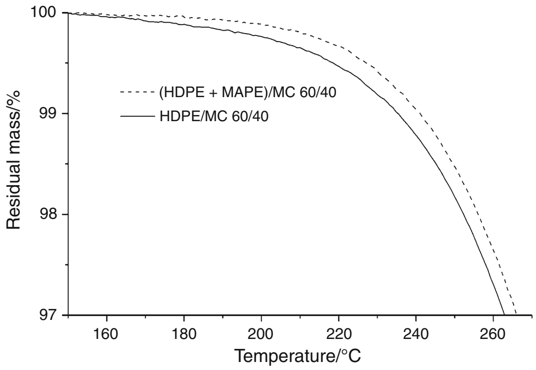

**Fig. 3** TG traces of compatibilized and uncompatibilized composites containing 40 mass/% of MC, recorded at 2 °C min$^{-1}$ heating rate

As concerning the effect of the compatibilization, TG curves of compatibilized and uncompatibilized composites are similar, unless little differences can be evidenced at low heating rates. In Fig. 3 TG traces of HDPE/MC 60/40 and (HDPE + MAPE)/MC 60/40 are reported (heating rate

**Table 2** Thermal decomposition temperature values of HDPE, MC, uncompatibilized, and compatibilized composites, recorded at normalized conversion degree of 0.025 and 0.200, at heating rate 2 °C min$^{-1}$ and at extrapolated heating rate 0 °C min$^{-1}$

| Samples | Heating rate 2 °C min$^{-1}$ | | Extrapolated values at heating rate 0 °C min$^{-1}$ (coefficient of determination values $r^2$ in parentheses) | |
|---|---|---|---|---|
| | $T_{d\ (\alpha=0.025)}$$^{a}$/°C | $T_{d\ (\alpha=0.200)}$$^{a}$/°C | $T_{d\ (\alpha=0.025)}$/°C | $T_{d\ (\alpha=0.200)}$/°C |
| HDPE | 388.6 | 424.7 | 365.2 ± 3.2 (0.990) | 405.0 ± 2.5 (0.997) |
| MC | 255.2 | 309.8 | 245.4 ± 0.7 (0.999) | 299.9 ± 0.6 (0.999) |
| HDPE/MC 60/40 | 231.9 | 288.0 | 224.1 ± 3.3 (0.989) | 277.9 ± 1.6 (0.993) |
| (HDPE + MAPE)/MC 60/40 | 236.2 | 288.4 | 225.9 ± 1.2 (0.996) | 277.7 ± 2.2 (0.991) |
| HDPE/MC 40/60 | 236.8 | 291.3 | 226.1 ± 2.1 (0.987) | 280.3 ± 1.2 (0.996) |
| (HDPE + MAPE)/MC 40/60 | 237.4 | 291.6 | 228.8 ± 0.2 (1.000) | 281.3 ± 2.3 (0.992) |

[a] Average values. Standard deviation values range between 0.6 and 2.1 °C

2 °C min$^{-1}$), showing the first stages of the thermal degradation process. As it can be observed, for composites compatibilized with MAPE the degradation process is slightly shifted at higher temperature values. At the highest MC content (60 mass/%), these differences become still lower.

These findings are in contradiction with results recently obtained by Araujo et al. [29], which report that the presence of a maleated coupling agent contributes to decrease the thermal stability of cellulose-containing composites. Instead, in our case no negative effects of the compatibilization have been found. On the contrary, it seems that a stronger interfacial adhesion is able to induce a slight but verifiable increase of the thermal stability of composites. This disagreement could perhaps be explained by considering that the maleic anhydride content of the coupling agent used by Araujo et al. is up to 5 times higher with respect to MAPE used in this study, thus letting to predict that only highly maleated polyolefins could actually compromise the thermal stability of cellulose-containing composites.

## A new approach for the kinetic analysis for NFR composites

In order to contribute to a deeper comprehension of the role of the cellulose component within the composite and on the effect of the compatibilization on the thermal degradation of NFR composites, the apparent activation energy was calculated by applying the Friedman, Flynn–Wall–Ozawa, and modified Coats–Redfern methods (Eqs. 6, 7, and 8, respectively).

In order to calculate $E_a$ for the thermal decomposition process, the estimation of conversion degree ($\alpha$) values has been performed on the basis of the following considerations. A few data are reported in literature on the activation energy of the thermal decomposition process of polyolefin-based composites reinforced with cellulose fillers and in all cases, for the calculation of $\alpha$ values, the thermal decomposition process of a composite sample is treated as a single process [15]. Nevertheless, this approach does not take into account the experimental indication that the first steps of decomposition of hemicellulose/cellulose components occur in a temperature range well separated from the decomposition range of the polyolefin matrix. Starting from this evidence, a more significant method for the evaluation of thermal decomposition kinetic parameters of cellulose in uncompatibilized and compatibilized composites was proposed in this study. In order to evaluate the conversion degree values $\alpha$ of the thermal decomposition process of the cellulose component, for composite samples and for MC, the residual mass was normalized with respect to the real cellulose content, following the equation:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \times X_{\mathrm{CELL}} \tag{9}$$

where $X_{\mathrm{CELL}}$ is the cellulose mass fraction within the sample.

With this procedure, normalized $\alpha$ values correspond to the conversion of the cellulose phase, independently from the relative amount of the polyolefin matrix. Normalized $\alpha$ values in this study range between 0 and 0.200, with steps of 0.025. Instead, for neat HDPE, whose results are reported for comparison, $\alpha$ values are calculated following Eq. 2.

In Table 2 a comparison between thermal decomposition temperature values recorded for normalized

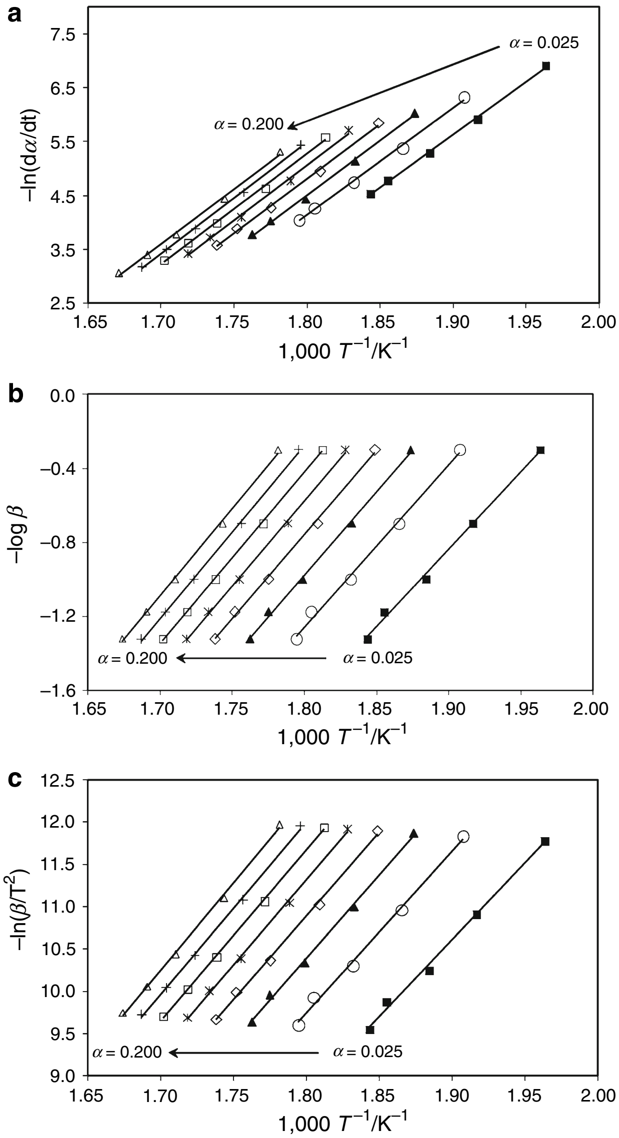

**Fig. 4** Isoconversional plots for the thermal decomposition of the cellulose component in (HDPE + MAPE)/MC 60/40, based on: **a** Friedman method (Eq. 6); **b** Flynn–Wall–Ozawa method (Eq. 7); **c** modified Coats–Redfern method (Eq. 8)

conversion degrees $\alpha = 0.025$ and $\alpha = 0.200$ is reported for measurements carried out at the lowest heating rate (2 °C $\min^{-1}$). Moreover, thermal decomposition values extrapolated at $\beta \rightarrow 0$ are also reported for the same conversion degrees. Extrapolated values have been calculated assuming a logarithmic relationship between $\beta$ and $T$ (see Eq. 7). As it can be observed, also in this case the compatibilization does not induce negative effects on the thermal stability of the cellulose component.

As an example, in Fig. 4 typical isoconversional plots of the compatibilized sample containing the lowest amount of MC ((HDPE + MAPE)/MC 60/40) are shown, based on the Friedman method (Fig. 4a), the Flynn–Wall–Ozawa (Fig. 4b), and the modified Coats–Redfern method (Fig. 4c). All the other investigated samples show a similar trend.

Apparent activation energy values ($E_a$) obtained by all the applied methods are summarized in Table 3 for normalized conversion values $\alpha = 0.1$ and $\alpha = 0.2$ together with the pre-exponential factors, calculated by the modified Coats–Redfern method. $E_a$ values are also graphed in Fig. 5.

As it can be observed, pre-exponential factor values for uncompatibilized and compatibilized composites range between A values of neat HDPE and MC, compatibilized composites showing higher A values with respect to uncompatibilized composites, either at $\alpha = 0.100$ or at $\alpha = 0.200$.

As concerning the activation energy, apart from numerical differences in $E_a$ values, the trend is similar for all the applied models. Neat HDPE and MC cellulose show, respectively, the lowest and the highest Ea values for the thermal decomposition process within the whole range of investigated conversion degree values. As concerning composite samples, it can be observed that at the lowest MC content (40 mass/%) the cellulose fraction undergoes to a significant decrease of the energy needed to initiate the thermal decomposition process with respect to the reference (cellulose in MC). By increasing the amount of cellulose phase (60 mass/% of MC), the apparent activation energy shifts to higher values, tending to be more similar to that shown by cellulose in MC.

Nevertheless, by comparing uncompatibilized and compatibilized composites, for both the investigated compositions and within the whole range of examined conversion values, activation energy values of compatibilized systems are higher with respect to $E_a$ values shown by uncompatibilized composites. This finding let to conclude that an improved interfacial adhesion between the hosting matrix and the fibrous reinforcement is able to increase the energy barrier needed to initiate the cellulose thermal decomposition process in cellulose-containing composites. In fact, during thermal decomposition of cellulose within a composite, degradation products are originated, at least in the first stages, at the cellulose-polymer interface [30]. Therefore, a stronger cellulose/polymer interfacial adhesion is able to protect the cellulose surface, thus contributing to slow down the overall cellulose decomposition process.

As concerning the influence of the cellulose amount on its thermal stability in composites, the apparent activation energy for the thermal decomposition process of the cellulose component has been found to decrease by increasing the amount of the polymer matrix. A possible justification

**Table 3** Apparent activation energy ($E_a$) obtained by the Friedman (F), Flynn–Wall–Ozawa (FWO), and modified Coats–Redfern (CR) methods for conversion degree values $\alpha = 0.1$ and $\alpha = 0.2$ and pre-exponential factor ($A$) obtained by the modified Coats–Redfern (CR) method

| Samples | F method | | FWO method | | CR method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E_a$/kJ $\mathrm{mol}^{-1}$ | | $E_a$/kJ $\mathrm{mol}^{-1}$ | | $E_a$/kJ $\mathrm{mol}^{-1}$ | $A/\min^{-1}$ | $E_a$/kJ $\mathrm{mol}^{-1}$ | $A/\min^{-1}$ |
| | $\alpha = 0.1$ | $\alpha = 0.2$ | $\alpha = 0.1$ | $\alpha = 0.2$ | $\alpha = 0.1$ | | $\alpha = 0.2$ | |
| HDPE | 134 ± 12<br>(0.991) | 146 ± 8<br>(0.993) | 147 ± 7<br>(0.989) | 159 ± 6<br>(0.992) | 142 ± 7<br>(0.994) | $5.2*10^{8}$ | 155 ± 7<br>(0.995) | $6.6*10^{9}$ |
| MC | 191 ± 7<br>(0.995) | 199 ± 3<br>(1.000) | 182 ± 5<br>(0.996) | 192 ± 4<br>(0.998) | 182 ± 6<br>(0.998) | $8.7*10^{14}$ | 191 ± 4<br>(0.999) | $3.9*10^{15}$ |
| HDPE/MC 60/40 | 161 ± 4<br>(0.998) | 168 ± 7<br>(0.996) | 159 ± 8<br>(0.992) | 165 ± 6<br>(0.995) | 158 ± 7<br>(0.995) | $2.1*10^{13}$ | 164 ± 6<br>(0.997) | $4.3*10^{13}$ |
| (HDPE + MAPE)/MC 60/40 | 168 ± 4<br>(0.998) | 173 ± 3<br>(0.999) | 165 ± 4<br>(0.998) | 172 ± 3<br>(0.999) | 164 ± 4<br>(0.999) | $1.1*10^{14}$ | 171 ± 3<br>(0.998) | $2.4*10^{14}$ |
| HDPE/MC 40/60 | 174 ± 6<br>(0.997) | 181 ± 4<br>(0.999) | 169 ± 8<br>(0.991) | 173 ± 4<br>(0.997) | 169 ± 7<br>(0.995) | $2.2*10^{14}$ | 173 ± 5<br>(0.998) | $2.7*10^{14}$ |
| (HDPE + MAPE)/MC 40/60 | 181 ± 4<br>(0.999) | 187 ± 6<br>(0.997) | 180 ± 2<br>(0.999) | 185 ± 3<br>(0.999) | 179 ± 2<br>(1.000) | $6.5*10^{14}$ | 184 ± 3<br>(1.000) | $1.2*10^{15}$ |

Coefficient of determination values $r^2$ in parentheses

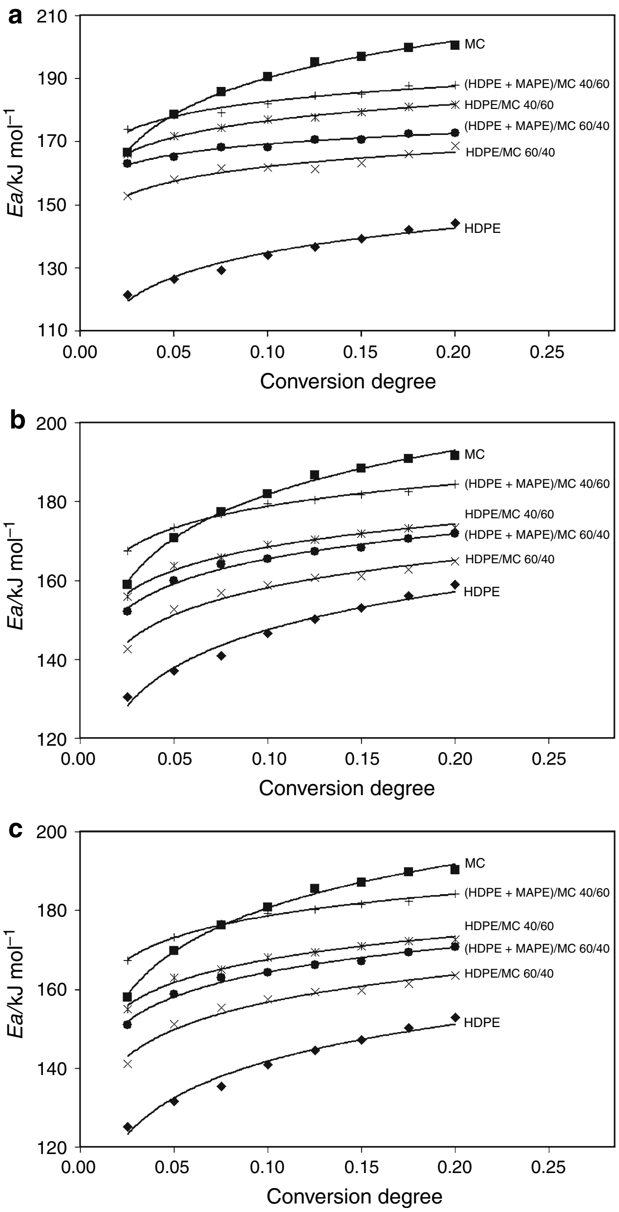

**Fig. 5** Apparent activation energy ($E_a$) for the thermal decomposition processes obtained from the Friedman (**a**), Flynn–Wall–Ozawa (**b**), and modified Coats–Redfern (**c**) methods for normalized conversion degree values ranging between 0.025 and 0.200

of this behavior can be found by considering that the rate of thermal degradation of cellulose depends on whether degradation products are quickly removed from the system or they remains in contact with the decomposing cellulose. In particular, the prolonged presence of degradation products within the system can accelerate the overall cellulose decomposition process [30]. In the case of NFR composites, during the first stages of the decomposition, degradation products must diffuse through the polymer matrix before flowing out from the system. Therefore, the presence of the molten polymer matrix can significantly slow down the removal of the degradation products from the system, thus prolonging their permanence within the system and explaining the trend above evidenced for the activation energy as a function of the cellulose/matrix ratio.

Moreover, another possible concomitant effect of the presence of the polymer is that a continuous phase, such as the molten matrix, is able to contribute to the transfer of free radicals among cellulose macromolecular chains. A free-radical-based decomposition mechanism of cellulose in cellulose-containing composites under non-oxidative conditions has been proposed and confirmed by Shafizadeh and Bradbury [31]. During this process the degradation products can react with the molten polymer via radical reactions, increasing the concentration of radical species within the system. Such an increase can contribute to induce a further decrease of the barrier energy for the decomposition process of the cellulose component. By admitting the reliability of these synergistic effects, involving the participation of the polymer matrix to the decomposition mechanism of the cellulose component either as a barrier against the quick removal of degradation products or as an effective medium for radical reactions, it would result well explained why the activation energy for the cellulose decomposition process in cellulose-containing composites results increased by reducing the matrix amount.

## Conclusions

The influence of cellulose content and fibers/matrix compatibilization on the thermal decomposition process of cellulose fibers in HDPE-based composites has been clarified by applying three model-free methods to dynamic thermogravimetric data collected on compatibilized and uncompatibilized composites. In particular, a new approach for the evaluation of thermal decomposition kinetic parameters of cellulose in uncompatibilized and compatibilized composites was developed. In order to evaluate the conversion values $\alpha$ of the thermal decomposition process of the cellulose component in cellulose-containing composites, the residual mass was normalized with respect to the real cellulose content.

As concerning the compatibilization, it has been evidenced an increase of the cellulose thermal stability as a consequence of the improved interfacial adhesion between the components in NFR composites. Within the whole range of examined conversion degrees, $E_a$ values in compatibilized systems are higher with respect to $E_a$ values calculated for uncompatibilized composites.

Moreover, the influence of the matrix/cellulose mass ratio on the thermal stability of cellulose was also analyzed: $E_a$ for the thermal decomposition process of the cellulose component decreases by increasing the amount of the polymer matrix. This behavior let to confirm a synergistic degradation mechanism that involves the participation of the polymer matrix to the decomposition mechanism of the cellulose fraction. The molten matrix acts either as a barrier against the quick removal of degradation products or as an effective medium for radical reactions.

## References

1. Bogoeva G, Avella M, Malinconico M, Buzarovska A, Grozdanov A, Gentile G, Errico ME. Natural fiber eco-composites. Polym Compos. 2007;28(1):98–107.
2. Joshia SV, Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? J Compos A. 2004;35:371–6.
3. Avella M, Casale L, Dell'Erba R, Focher B, Martuscelli E, Marzetti A. Broom fibers as reinforcing materials for polypropylene-based composites. J Appl Polym Sci. 1997;68(7):1077–89.
4. Awal A, Ghosh SB, Sain M. Thermal properties and spectral characterization of wood pulp reinforced bio-composite fibers. J Therm Anal Calorim. 2010;99(2):695–701.
5. Bouza R, Marco C, Ellis G, Martín Z, Gómez MA, Barral L. Analysis of the isothermal crystallization of polypropylene/wood flour composites. J Therm Anal Calorim. 2008;94(1):119–27.
6. Huda MS, Mohanty AK, Drzal LT, Schut E, Misra M. Composite materials "Green" composites from recycled cellulose and poly(lactic acid): physico-mechanical and morphological properties evaluation. J Mater Sci. 2005;40:4221–9.
7. Baroulaki I, Mergos JA, Pappa G, Tarantili PA, Economides D, Magoulas K, Dervos CT. Performance of polyolefin composites containing recycled paper fibers. Polym Adv Technol. 2006; 17(11–12):954–66.
8. Ambrose CA, Hooper R, Potter AK, Singh MM. Diversion from landfill: quality products from valuable plastics. Resour Conserv Recycl. 2002;36(4):309–18.
9. Avella M, Avolio R, Bonadies I, Carfagna C, Errico ME, Gentile G. Recycled multilayer cartons as cellulose source in HDPE based composites: compatibilization and structure-properties relationships. J Appl Polym Sci. 2009;114(5):2978–85.
10. Joly C, Kofman M, Gauthier R. Polypropylene/cellulosic fiber composites: chemical treatment of the cellulose assuming compatibilization between the two materials. J Macromol Sci Pure Appl Chem. 1996;33(12):1981–96.
11. Keener TJ, Stuart RK, Brown TK. Maleated coupling agents for natural fibre composites. J Compos A. 2004;35:357–62.
12. Avella M, Bogoeva-Gaceva G, Bužarovska A, Errico ME, Gentile G, Grozdanov A. Poly(lactic acid)-based biocomposites reinforced with kenaf fibers. J Appl Polym Sci. 2008;108:3542–51.
13. Avella M, Bogoeva-Gaceva G, Bužarovska A, Errico ME, Gentile G, Grozdanov A. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) based biocomposites reinforced with kenaf fibres. J Appl Polym Sci. 2007;104:3192–200.
14. Song B, Wang Y, Bai H, Liu L, Li Y, Zhang J, Zhou Z. Crystallization and melting behaviors of maleic anhydride grafted poly(propylene) nucleated by an aryl amide derivative. J Therm Anal Calorim. 2010;99(2):563–70.
15. Kim H-S, Yang H-S, Kim H-J, Park H-J. Thermogravimetric analysis of rice husk flour filled thermoplastic polymer composites. J Therm Anal Calorim. 2004;76:395–404.
16. Bajer K, Kaczmarek H, Dzwonkowski J, Stasiek A, Ołdak D. Photochemical and thermal stability of degradable PE/paper waste composites obtained by extrusion. J Appl Polym Sci. 2007;103:2197–206.
17. Beg MDH, Pickering KL. Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites. Polym Degrad Stab. 2008;93:1939–46.
18. Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. J Polym Sci Polym Symp. 1964;6(1):183–95.
19. Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci Polym Lett. 1966;4(5):323–8.
20. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature. 1964;201:68–72.
21. Sclavons M, Carlier V, De Roover B, Franquinet P, Devaux J, Legras R. The anhydride content of some commercial PP-g-MA: FTIR and titration. J Appl Polym Sci. 1996;62(8):1205–10.
22. Rodgers JL, Nicewander WA. Thirteen ways to look at the correlation coefficient. Am Stat. 1988;42:59–66.
23. Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn. 1965;38(11):1881–6.
24. Achilias DS, Karabela MK, Sideridou ID. Thermal degradation and isoconversional kinetic analysis of light-cured dimethacrylate copolymers. J Therm Anal Calorim. 2010;99(3):917–23.
25. Ernesto Fischer P, Jou CS, Gokalgandhi SS. Obtaining the kinetic parameters from thermogravimetry using a modified Coats and Redfern technique. Ind Eng Chem Res. 1987;26(5):1037–40.
26. Bigger SW, Scheirs J, Camino G. An investigation of the kinetics of cellulose degradation under non-isothermal conditions. Polym Degrad Stab. 1988;62:33–40.
27. Soares S, Camino G, Levchikt S. Comparative study of the thermal decomposition of pure cellulose and pulp paper. Polym Degrad Stab. 1995;49:275–83.
28. Scheirs J, Camino G, Tumiatti W. Overview of water evolution during the thermal degradation of cellulose. Eur Polym J. 2001;37:933–42.
29. Araujo JR, Waldman WR, De Paoli MA. Thermal properties of high density polyethylene composites with natural fibres: coupling agent effect. Polym Degrad Stab. 2008;93:1770–5.
30. Sapieha S, Pupo JF, Schreiber HP. Thermal degradation of cellulose-containing composites during processing. J Appl Polym Sci. 1989;37:233–40.
31. Shafizadeh F, Bradbury AGW. Thermal degradation of cellulose in air and nitrogen at low temperature. J Appl Polym Sci. 1979;23:1431–42.