Composites: Part B 73 (2015) 139–148

Contents lists available at ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Effects of sepiolite clay on degradation and fire behaviour of a bisphenol A-based epoxy

Aldobenedetto Zotti, Anna Borriello *, Mariarosaria Ricciardi, Vincenza Antonucci, Michele Giordano, Mauro Zarrelli

Institute of Polymers, Composites and Biomaterials, National Research Council of Italy, P.le Fermi, 1, 80055 Portici, Naples, Italy

ARTICLE INFO

Article history:
Received 4 November 2014
Received in revised form 2 December 2014
Accepted 9 December 2014
Available online 16 December 2014

Keywords:
A. Polymer-matrix composites (PMCs)
A. Thermosetting resin
B. Thermal properties
Sepiolite

ABSTRACT

As-received and pre-treated sepiolite/epoxy systems, characterised by an inorganic content from 2 to 10 wt.%, were investigated in order to assess induced-filler effect on degradation and fire behaviour.

Thermogravimetrical results show that the thermal stability of the hosting epoxy, is slightly affected by the presence of sepiolite for both typologies; whereas, changes induced in char morphology by the pre-treated clay will significantly affect the fire behaviour of the final nanocomposite.

Modelling of thermo-gravimetrical results in air atmosphere, by means of Kissinger procedure, shows a noteworthy reduction of activation energies associated with each degradation steps, especially at highest sepiolite content either by using as-received and pre-treated inorganic filler. This substantially indicates that the presence of sepiolite shorten the whole degradation process on the temperature scale. On the other hand, the different morphology of the char layer during the burning process can have relevant flame retardant effects acting on both condensate and vapour phase. Analysing the cone calorimetric data, a reduction of about 27% of the peak of heat release rate for the highest sepiolite percentage is measured and the burning total period is increased thus confirming that sepiolite when pre-treated represents a valid fire retardant inorganic filler for such a system.

1. Introduction

Epoxy resins have many advantages, as low specific weight compared to metals, high mechanical properties and high corrosion resistance and they are the most commercially successful thermosetting materials, especially as structural adhesives, high-performance protective coatings and matrices of composite materials [1,2]. However epoxy resins have low fire resistance and produce toxic smokes during combustion. Moreover these materials are brittle, having limited utility in applications that require high fracture toughness. The extensive applications of epoxy resins motivate intense studies aiming to prepare organic–inorganic nanocomposites with novel and improved performances, like fire and smoke retardancy. Two distinct stages, respectively, condensed and vapour phase processes, interact synergistically to draw the complex phenomenon of combustion. In order to enhance the fire resistance of a material, flame retardants take actions on vapour phase by diluting the oxidising elements or the pyrolysis products, and/or on the condensed phase by promoting, ad example, the intumescences or the formation of a compact char. In particular, a compact char on the material surface acts as protective barrier, which reduces the volatiles flow and heat exchange between flame and bulk degrading material [3]. Addition of inert inorganic filler is a simple and cost-effective solution to promote the flame retardancy potentially suitable to dilute the combustible in the solid and vapour phases, and promote the formation of a compact char.

As polymers are characterised by a low cost, also the approach to enhance the mechanical and fire resistance of the system must be affordable: it has been found that the clays are good candidate to improve the property of polymers, as they are inexpensive and easily processable with polymers. For this reason, during last years, polymer/clay nanocomposites have obtained a great attention either as research topic and for industrial outcome [4,5]. In fact, low quantity of clay, as polymer filler, can significantly improve the mechanical and thermal properties of the neat material. However the level of property enhancement can strongly depends upon different factors such as particle content, dimensions, geometrical shape and degree of dispersion. For instance, composites filled with micrometric size particles show reduced mechanical and thermal properties if compared to composites filled with nanometric size particles [5]. The geometrical configuration, their dimensional ratio

---

* Corresponding author. Tel.: +39 0817758814; fax: +39 0817758850.
E-mail address: borriell@unina.it (A. Borriello).

http://dx.doi.org/10.1016/j.compositesb.2014.12.019
1359-8368/

and the dispersion achieved surely affect the final property of the hosting system even if a similar loading content is considered [6]

Clays have been often used as filler to improve the fire behaviour of polymer. Duquesne et al. obtained a reduction by 25% and 50% of PHRR, respectively adding Cloisite Na+ and Cloisite 30B in an Ethylene–vinyl acetate matrix [7]. A similar trend has been observed by Samyn et al. that analysed the fire behaviour of a polyamide modified with montmorillonite: moreover, they demonstrated that if nanodispersion is achieved, polymer/clay nanocomposites should exhibit fire retardant properties, independently by clay nano-morphology in the matrix [8].

Surely, among the different clay, candidate for nanocomposite production, sepiolite can be valuable nanofiller. Sepiolite is a fibrous magnesium phyllosilicate, whose ideal formula is $[Si_{12}Mg_8O_{30}(OH)_4](H_2O)_4{\cdot}8H_2O$. Its structure is formed by two layers of silica tetrahedrons linked by a layer of magnesium ions in octahedral coordination. The octahedral sheets are not continuous like in the other phyllosilicates: this structure provides infinite channels along the fibre axis with a cross section of about $1 \times 0.4\ \text{nm}^2$ [9,10]. The presence of these channels strongly increases the specific surface area of these particles, up to 200–300 m^2/g. By using this large specific surface area, sepiolite clay is used in rheological, sorptive and catalytic applications [9].

In this work, sepiolite nanopowder was used as a reinforcement filler of a bisphenol A-based epoxy system to investigate the induced difference on thermal and fire behaviour compared to the neat materials. Hosting polymer and its sepiolite filled nanocomposite were examined by performing mainly thermogravimetric analysis (TGA) and cone calorimeter. The dispersion of the clay in the epoxy matrix has been analysed by optical and SEM microscopy, to assess the level of dispersion achieved and its homogeneity.

2. Experimental section

2.1. Materials

In this work, the matrix used is a bisphenol-A/epichlorohydrin derived liquid epoxy resin (EPON™ Resin 828) supplied by Hexion. The system is characterised by an equivalent weight (EEW) of 188 g/mol and a room temperature (25 °C) viscosity of about 10–15 Pa s [11]. The used curing agent was a Triethylene Tetramine (TETA), commercially known as EPIKURE3234, which is a polyamine with an amine hydrogen equivalent weight (AHEW) of 1.41–1.46 mg/g [12]. This curing agent provides low viscosity with high performance properties after a relatively low temperature cure. Sepiolite was gently provided by Mi.Mac. (Capua, Italy) and it was used in different concentrations as inorganic filler in two different forms: hydrated (as-received or IDRA) and dehydrated (i.e. pre-treated or ANIDRA). Pre-treatment of the received sepiolite was carried out in order to remove all traces of moisture absorbed by the clay during micronisation and handling operations. The dehydration pre-stage was carried out by holding the powder filler at isothermal temperature (100 °C) in oven for 3 h under vacuum; after this stage, the inorganic filler was stored in a desiccator.

The mixing of epoxy resin and sepiolite was performed by tip sonication using a Misonix S3000 sonicator set at 30 W power for 1 h. An oil bath was employed to hold the mixture at 50 °C. The mixture was degassed in a planetary mixer (Thinky Mixer ARV-310) at the velocity of 2000 rpm under vacuum for 5 min. The curing agent (EPIKURE3234) was then added to the degassed mixture, with a ratio of 100:13 phr. Mixing of sepiolite/epoxy mixture and hardener (EPIKURE 3234) was performed by planetary mixer at the velocity of 2000 rpm under vacuum for 1 min and then poured into a steel mould, which was coated previously with a release agent (FREKOTE 70).

The same curing cycle was assumed for all the manufactured sample plates, i.e. 1 h @ 70 °C followed by a post-curing stage of 2 h @ 120 °C. The cured plates were cooled down slowly, in the curing oven, over the night to room temperature, removed from the mould and cut to prescribed sample dimensions for the programmed fire tests.

2.2. Experimental methods

2.2.1. SEM and optical microscopy

SEM and optical micrographs of nanocomposites were taken respectively by an 1450VP LEO SEM microscopy and an optical Olimpus BX51 Instruments equipped with different magnitude oculars. Cured samples for SEM analysis were obtained by cryogenic rupture to prepare fracture surface. Samples observed by optical microscopy were prepared by operating a precise sawing machine at high speed rotation and constant thickness.

2.2.2. Thermogravimetrical analysis

Thermogravimetrical analysis (TGA) was performed using a TGA Q500 by TA Instruments under nitrogen atmosphere (50 mL/min) and a heating ramp of 10 °C/min. Sample weight of around 5 ± 0.5 mg were considered for each run test from ambient temperature to 800 °C. The precision on the temperature measurements during each scan, according to the calibration procedure was ± 0.5 °C in the range 30–400 °C and ±1 °C in the range 400–800 °C. The precision on the weight is ±0.01%.

2.2.3. Cone calorimeter analysis

The fire behaviour of the neat system and its filled mixture with sepiolite clay was investigated by cone calorimeter. All tests were performed using a Fire Testing Technology Ltd. equipment following the indication of the ASTM E1354-04 standard. The Conical Heater is wound in the form of a truncated cone, rated 5000 W at 230 V with a heat output of 100 kW/m^2. The mass measurements are conducted via a strain gauge load cell with an accuracy of 0.01 g. Heat release calculations were based on the oxygen consumption principle [13] implemented directly within the equipment software. The samples were square plates of $3 \times 100 \times 100$ mm in size.

From the cone calorimeter, some interesting parameters to evaluate the flammability behaviour and the smoke emission could be drawn out, in particular:

- The rate of released heat during the sample combustion per unit area, reported as HRR (heat release rate).
- The maximum value of the HRR, indicated as PHRR (peak heat release rate).
- The time integral of the HRR curve during the whole combustion, which correspond to the THR parameter (total heat released).

Analysing and comparing the experimentally obtained values and also computing indirect parameter such as the FIGRA index for the manufactured samples, the effect of sepiolite over the fire property of the neat epoxy system could be evaluated and discussed.

3. Results and discussion

3.1. Microscopy

The general morphology generated by tip-sonication mixing method in the sepiolite–epoxy network is reported and analysed in this paragraph. Samples were taken from prepared specimens in different locations and analysed by SEM and optical microscopy. In particular, optical analysis was used to evaluate the sepiolite dispersion level and its local distribution at all filler contents, whereas SEM microscopy was employed to verify the nominal dimensions of the sepiolite aggregates within the epoxy matrix.

Sepiolite clay is typically characterised by a needle-shaped geometry having nominal dimensions of about ten nanometers in

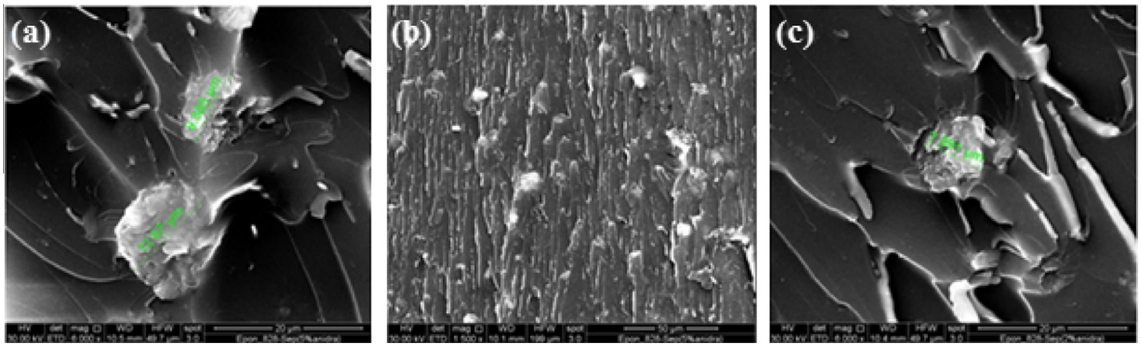

Fig. 1. SEM micrographics of 2 and 10 wt.% samples.

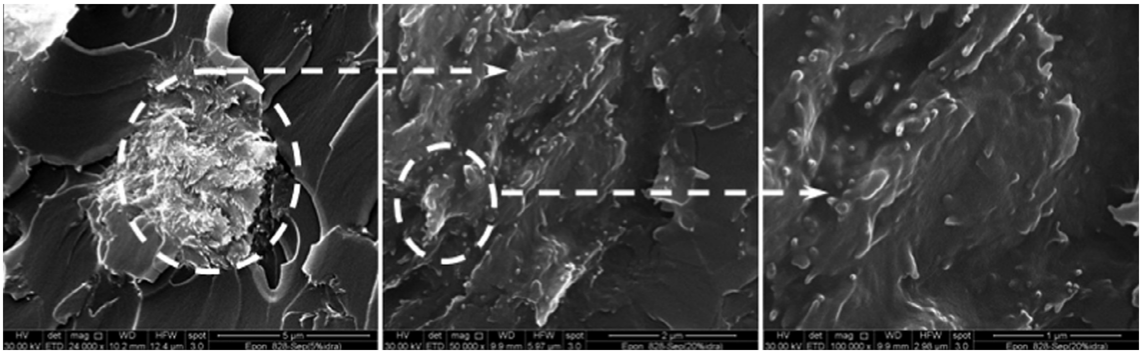

Fig. 2. Sepiolite round-shapes aggregate: zoom-in sequence of SEM image.

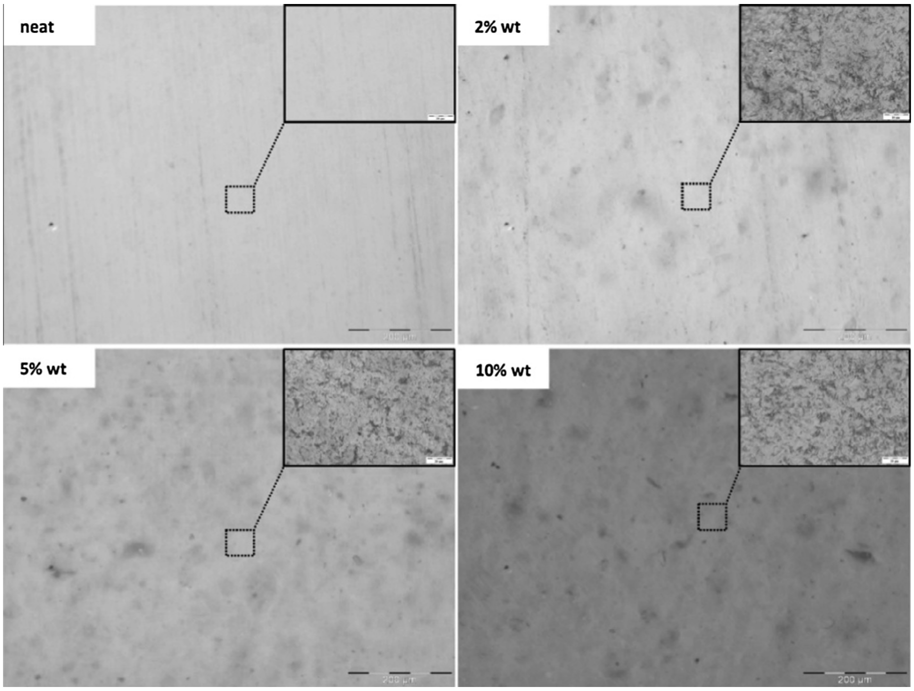

Fig. 3. Optical microscopy (20× and 50×) of neat and filled [14].

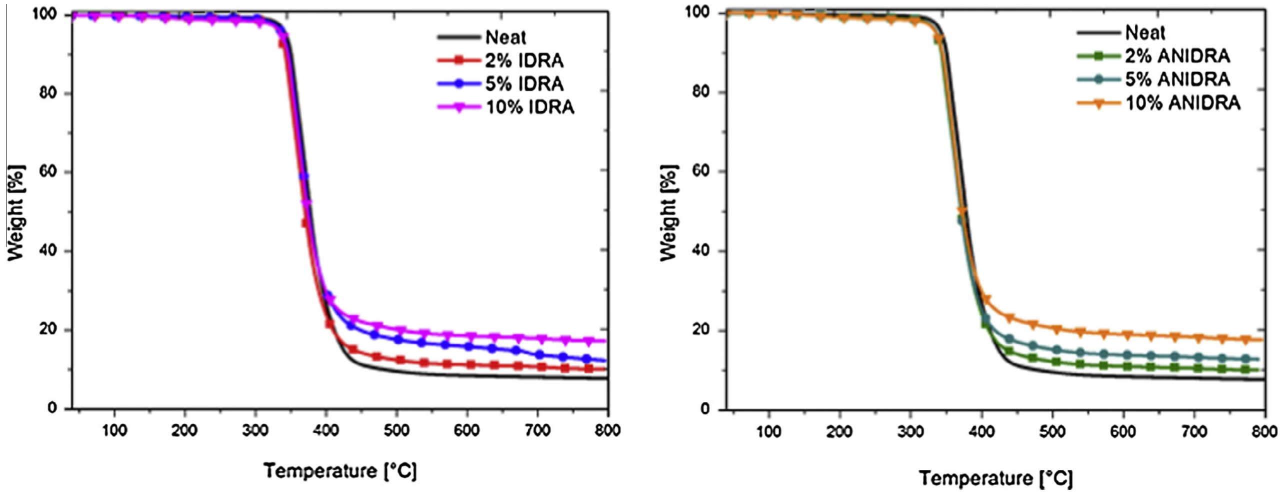

Fig. 4. TGA curves (inert atmosphere) of epoxy with 2, 5 and 10 wt.% of sepiolite hydrated (left) and dehydrated (right).

Table 1
TGA test results for the Epon828/sepiolite systems in inert atmosphere.

Sample	T_{onset} (°C)	$T_{end\ set}$ (°C)	T_{max} (°C)	Char yield (%)
Neat	344.8 ± 2.6	420.6 ± 4.5	366.2 ± 3.2	7.7 ± 0.1
2% sep anidra	337.6 ± 3.5	412.9 ± 3.7	358.9 ± 3.6	10.0 ± 0.2
2% sep idra	336.5 ± 3.2	416.1 ± 3.4	359.5 ± 3.1	10.1 ± 0.1
5% sep anidra	339.2 ± 3.6	409.9 ± 3.1	358.0 ± 2.2	12.7 ± 0.3
5% sep idra	341.7 ± 2.8	408.9 ± 3.1	362.8 ± 2.1	12.3 ± 0.5
10% sep anidra	339.4 ± 2.6	399.7 ± 3.8	361.8 ± 2.3	17.7 ± 0.1
10% sep idra	341.9 ± 2.7	405.4 ± 2.6	362.5 ± 1.7	17.2 ± 0.6

diameter and few microns in length [9]. Fig. 1 reports the sepiolite aggregates of few micrometres with a round-shaped geometry. Zooming in the formed micro-cluster, the typical needle-like geometry of singular sepiolite structure is observable (Fig. 2).

The optical micrographics for the samples with different amount of sepiolite are shown in Fig. 3 by using two different magnitudes, 20× and 50×. In all cases, the microscopy revealed an appreciable homogeneity of the filler within the hosting matrix and a submicron level of dispersion, even for the highest sepiolite content. The very few sepiolite bundles that remain within the matrix are likely due to the existing aggregates which were not broken up by the sonication mixing.

3.2. Thermal degradation: experimental results and Kissinger model

The effect of sepiolite content on the thermal stability and fire performance of epoxy system was investigated by thermo-gravimetric analysis and by cone calorimetry tests.

Fig. 4 shows TGA curves, in inert atmosphere, for the Epon828/sepiolite system in its both forms, hydrated and dehydrated. All systems exhibit thermal degradation and significant weight loss (higher than 80%) with temperature, following a single step degradation mechanism. With the exception of residues, which obviously change due to the content of inorganic filler (and water percentage) loaded within the hosting epoxy system, the presence of sepiolite negligibly influence the thermal stability of the system. Table 1 reports a summary of the main temperature values as measured by TGA tests. The onset and the end set of thermal degradation temperature were determined from the intersection of the two tangents; the peak degradation temperature was determined from the first derivative of the TGA curves (DTGA profiles).

It is clear that the char yield increases with the addition of the sepiolite. The found variation among the different samples is substantially depended over the filler percentage. Fig. 5 shows the thermo-gravimetrical profile of idra and anidra sepiolite powder.

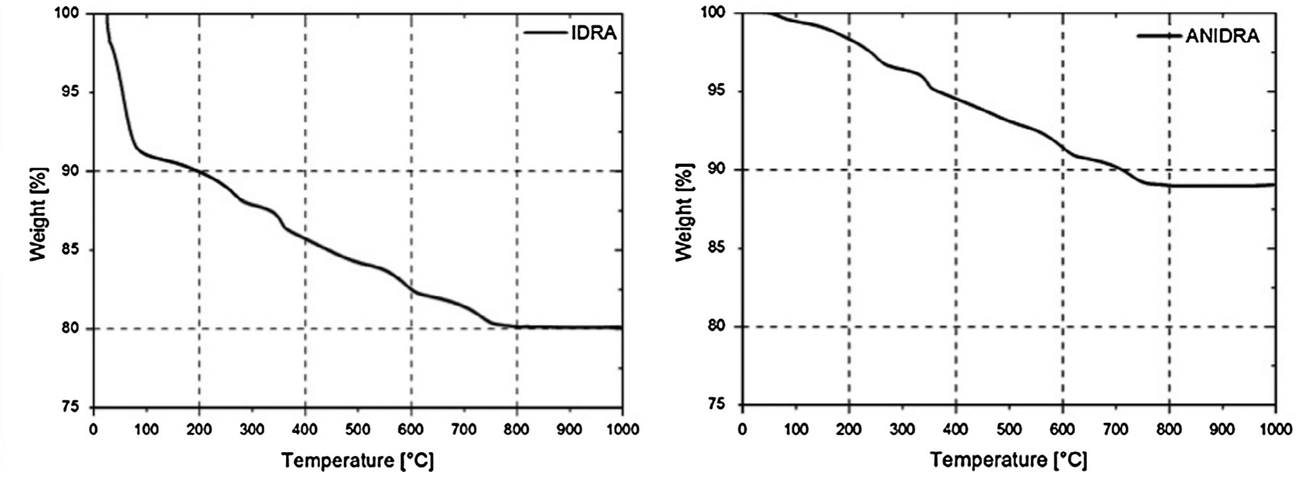

Fig. 5. Thermogravimetric analysis of pristine sepiolite hydrated (left) and dehydrated (right) samples.

It can be noted that the residual weight is very high in both cases, respectively 80% for idra and 89% for the dehydrated filler. The apparent difference of the residual weight finds a logical explanation if the mass loss related to the intake water of the as-received sepiolite is taken into account. In fact, slope variation of the idra curve around $T = 100$ °C, can be surely related to out-taken water weight which results equal to 9.2% of the initial sample mass. The corresponding curve for the pre-treated sepiolite, shows a negligible weight mass loss up to 100 °C (only 0.6%) due to the minimum amount of water still into the sample after the pre-treatment, along with a stable residual char at $T > 800$ °C. Two main evidences are brought out by the experimental results, (a) the pre-treatment (i.e. dehydration) act successfully in e direction of out-taken the absorbed water content from the sepiolite as received; (b) the weight residue of both typology of sepiolite is the same and stable for $T > 800°$.

Frost et al. work [15] reported thermal stability data of sepiolite clay, describing all the degradation reaction occurring during a dynamic heating which are very well in agreement with our findings.

Fig. 6 shows the degradation curves of the loaded epoxy computed on the effective weight of epoxy without sepiolite residue. Appreciable overlapping of the curves is achieved with a final almost constant level of residual char (about 8%). The increased char residue is surely due to the presence of the inert compound within the hosting system, which, not chemically interacting with the resin, does not influence the loss mass process.

By analysing the characteristic onset and end set temperature, it could be concluded that the sepiolite will eventually shift the degradation process at slightly lower temperature compared to the neat system. In fact, the degradation onset temperature is to some extent reduced in the presence of sepiolite (varying from 344.8 °C to 341.9 °C in the case of 10% filler content); a more remarkable reduction is found for the end-set temperatures which results almost 20 °C lower than neat epoxy in the case of highest sepiolite content (i.e. from 426.6 °C to 405.4 °C). These results find reasonable literature support as reported by Paterson-Jones et al. [16]. The usage of inorganic fillers could accelerate thermal decomposition of epoxies, probably due to catalyst effect of the filler or due the induced filler discontinuity into the final bulk system.

TGA tests were also performed in air. Fig. 7 shows TGA curves performed on the neat sample at 3 different heating rates (15 °C/min, 10 °C/min and 5 °C/min). The expected typical degradation behaviour of the epoxy resins, characterised by two main changes in slopes of the curve, is recorded. The first step (around 400 °C) mainly involves dehydration of the material and formation of a

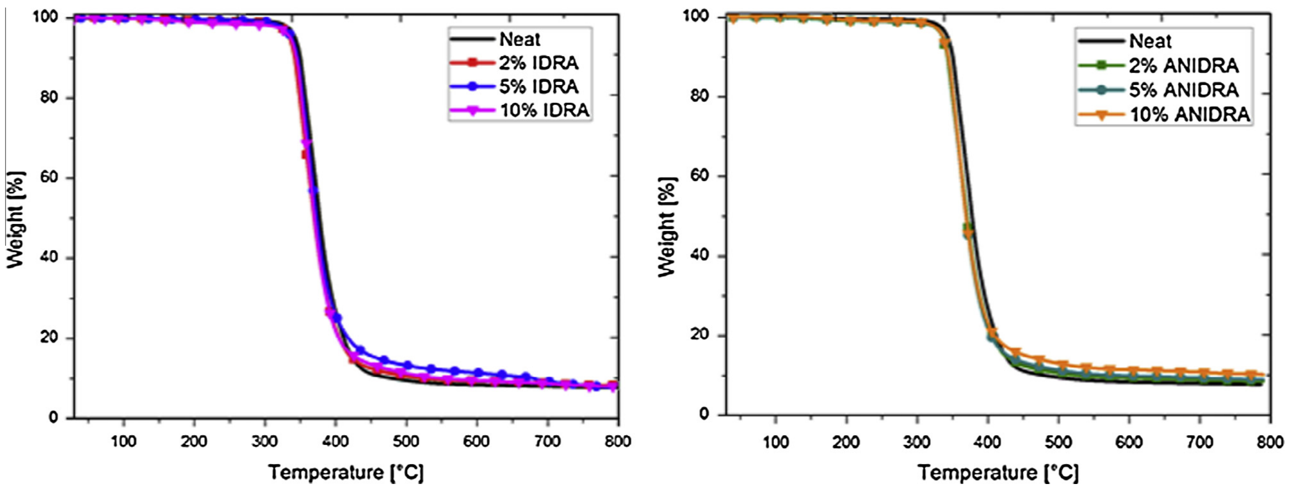

Fig. 6. Degradation curves of the samples filled with hydrated (left) and dehydrated (right) sepiolite, without sepiolite residue.

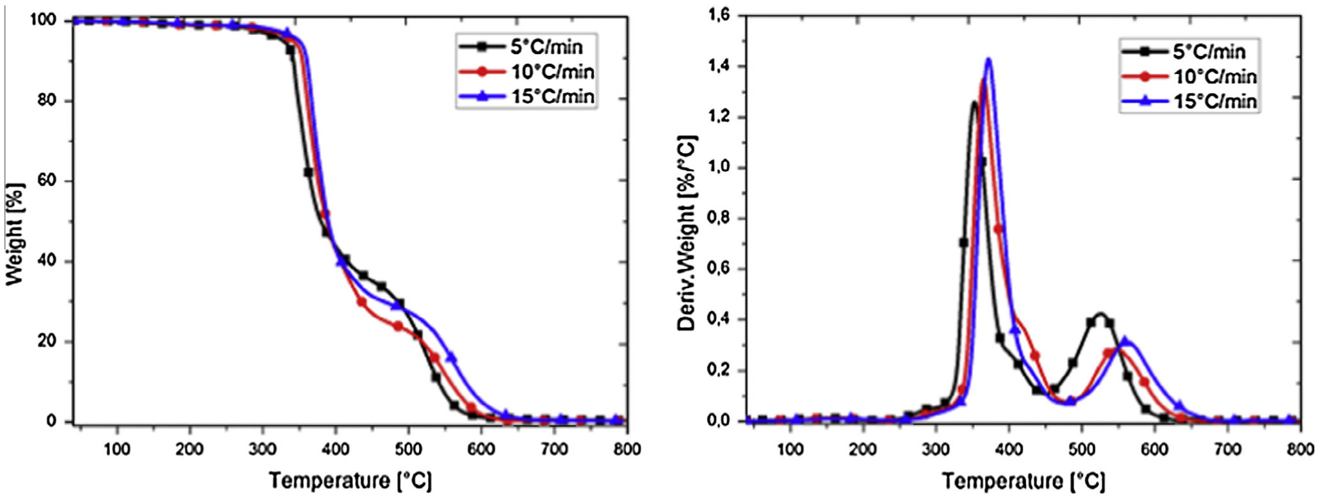

Fig. 7. TGA (left) and DTGA (right) curves of the neat epoxy system versus heating rates.

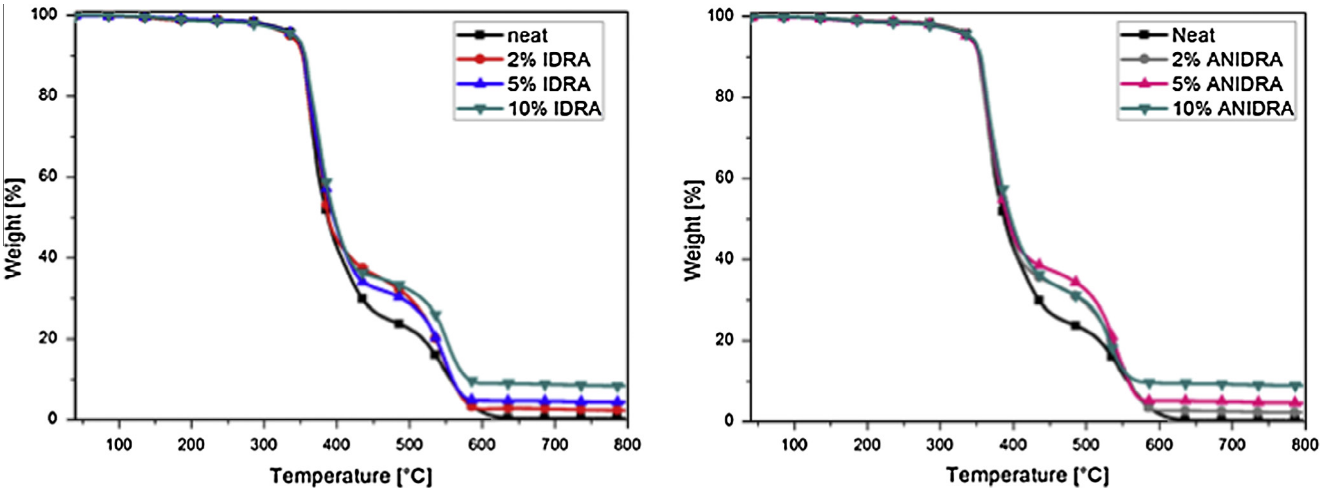

Fig. 8. TGA curves (air atmosphere) of epoxy with 2, 5 and 10 wt.% of sepiolite hydrated (left) and dehydrated (right).

polyaromatic structure. The second step corresponds to a thermo-oxidative reaction which leads to the complete degradation of the carbonaceous materials and char forming [17].

Fig. 8 shows TGA curves (heating rate 10 °C/min) relative to nanocomposites with different amount of hydrated (left) and dehydrated (right) sepiolite. As it is shown, the addition of sepiolite, in its both forms (hydrated and dehydrated), does not induce any changes of the degradation curve pattern confirming that sepiolite act as an inert filler without any chemical interaction with the hosting system.

Table 2 summarises the TGA results for the nanocomposite samples tested, in oxidative atmosphere, with a heating rate of 10 °C/min. The parameters, $T^{\text{Peak I}}$ and $T^{\text{Peak II}}$ correspond to the temperature of maximum weight loss in each degradation step, and they were calculated using DTGA curves.

Results of dynamic TGA tests could be suitably used to determine the activation energies of the oxidation process by using the Kissinger Method which can be employed to analyse the TGA data regardless any pre-assumption on thermal degradation mechanism.

For dynamic TGA measurements, mass loss is monitored as function of temperature at different heating rates and kinetics degradation in its general form can be modelled as:

$$\frac{d\alpha}{dt} = f(\alpha, T) \tag{1}$$

where T and α represents respectively, temperature and mass loos. Considering an nth order reaction mechanism and the degradation rate following Arrhenius temperature dependence, it can be written:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{2}$$

with

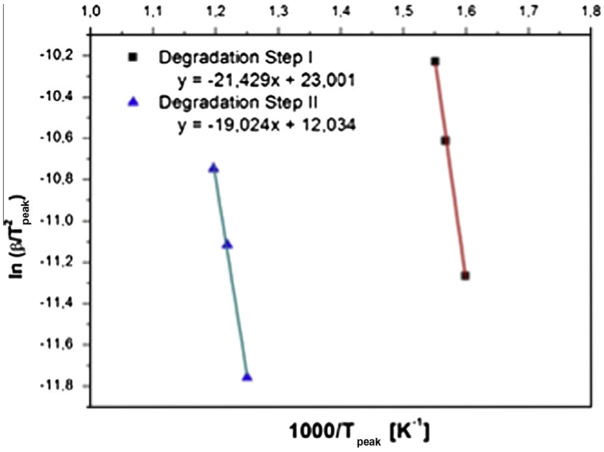

Fig. 9. Kissinger method applied to the neat sample.

Table 3
Kissinger activation energies for each degradation steps for the Epon828/sepiolite systems in air.

Sample	E_a^{I} (kJ/mol)	E_a^{II} (kJ/mol)
Neat	178.2	158.2
2% sep anidra	190.4	114.7
2% sep idra	166.3	133.4
5% sep anidra	184.9	117.5
5% sep idra	185.6	109.3
10% sep anidra	155.1	143.7
10% sep idra	112.4	130.4

$$k = A\exp\left(\frac{-E}{RT}\right) \tag{3}$$

The combination of (2) and (3) gives

Table 2
Results of TGA tests (in air) for the Epon828/sepiolite systems.

Sample	$T_{\text{end set I}}$ (°C)	$T_{\text{end set II}}$ (°C)	$T_{\text{Peak I}}$ (°C)	$T_{\text{Peak II}}$ (°C)	Char yield (%)
Neat	438.5 ± 3.1	592.8 ± 4.2	364.9 ± 2.1	547.0 ± 2.6	0.3 ± 0.1
2% sep anidra	410.4 ± 1.5	576.1 ± 3.6	370.5 ± 5.4	547.5 ± 3.8	2.3 ± 0.3
2% sep idra	391.8 ± 3.6	574.0 ± 4.2	363.9 ± 3.9	548.8 ± 2.3	2.36 ± 0.2
5% sep anidra	426.2 ± 2.7	565.7 ± 3.4	366.8 ± 2.4	542.2 ± 4.1	4.65 ± 0.5
5% sep idra	404.0 ± 3.1	569.9 ± 2.7	364.6 ± 3.8	548.5 ± 3.4	4.36 ± 0.6
10% sep anidra	421.7 ± 4.5	553.4 ± 3.3	370.6 ± 2.7	532.0 ± 2.1	8.95 ± 0.3
10% sep idra	416.8 ± 1.7	573.2 ± 2.4	366.0 ± 1.6	551.2 ± 3.1	8.38 ± 0.2

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(\frac{-E}{RT}\right) \tag{4}$$

If heating rate $\beta = dT/dt$ is constant, the variation in degree of conversion can be analysed as a function of temperature and this temperature being dependent on the time of heating:

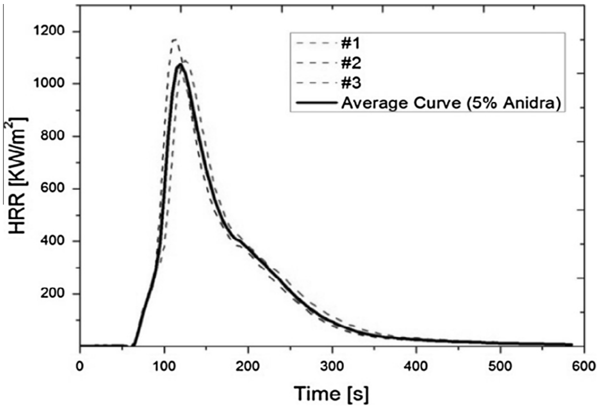

Fig. 10. HRR curves of the sample with 5% of dehydrated sepiolite and its average curve.

$$\frac{d\alpha}{dT} = \frac{A}{\beta}f(\alpha)\exp\left(\frac{-E}{RT}\right) \tag{5}$$

The integrated form of this equation generally is expressed as:

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

where $g(\alpha)$ is the integrated form of the conversion dependence function.

Kissinger's method analyzes the variations in the thermo-gravimetric data through the changes of run heating rate, β, as function of the maximum peak temperatures, $T_{\max}$ (in DTG curves) according to the following equation:

$$\ln\left(\frac{\beta}{T^2_{\max}}\right) = \left\{\ln\frac{AR}{E} + \ln\left[n(1-\alpha_{\max})^{n-1}\right]\right\} - \frac{E}{RT_{\max}} \tag{7}$$

where $T_{\max}$ is the temperature of inflection point of thermal degradation curves which corresponds to the maximum reaction rate; $\alpha_{\max}$ is the conversion at $T_{\max}$, and n is the reaction order. Assuming that $\boldsymbol{f'(\alpha_{\max}) = n(1-\alpha_{\max})^{n-1}} \approx \textbf{const}$ the activation energy $\boldsymbol{E}$ can be determined from a plot of $\ln(\beta/T^2_{\max})$ against $1/T_{\max}$.

Therefore, the activation energy for each degradation step was calculated from straight line fitting of $\ln(\beta/T^2_{\text{peak}})$ vs. $1/T^2_{\text{peak}}$ (see Fig. 9 for the neat system) according to the following equation [18]:

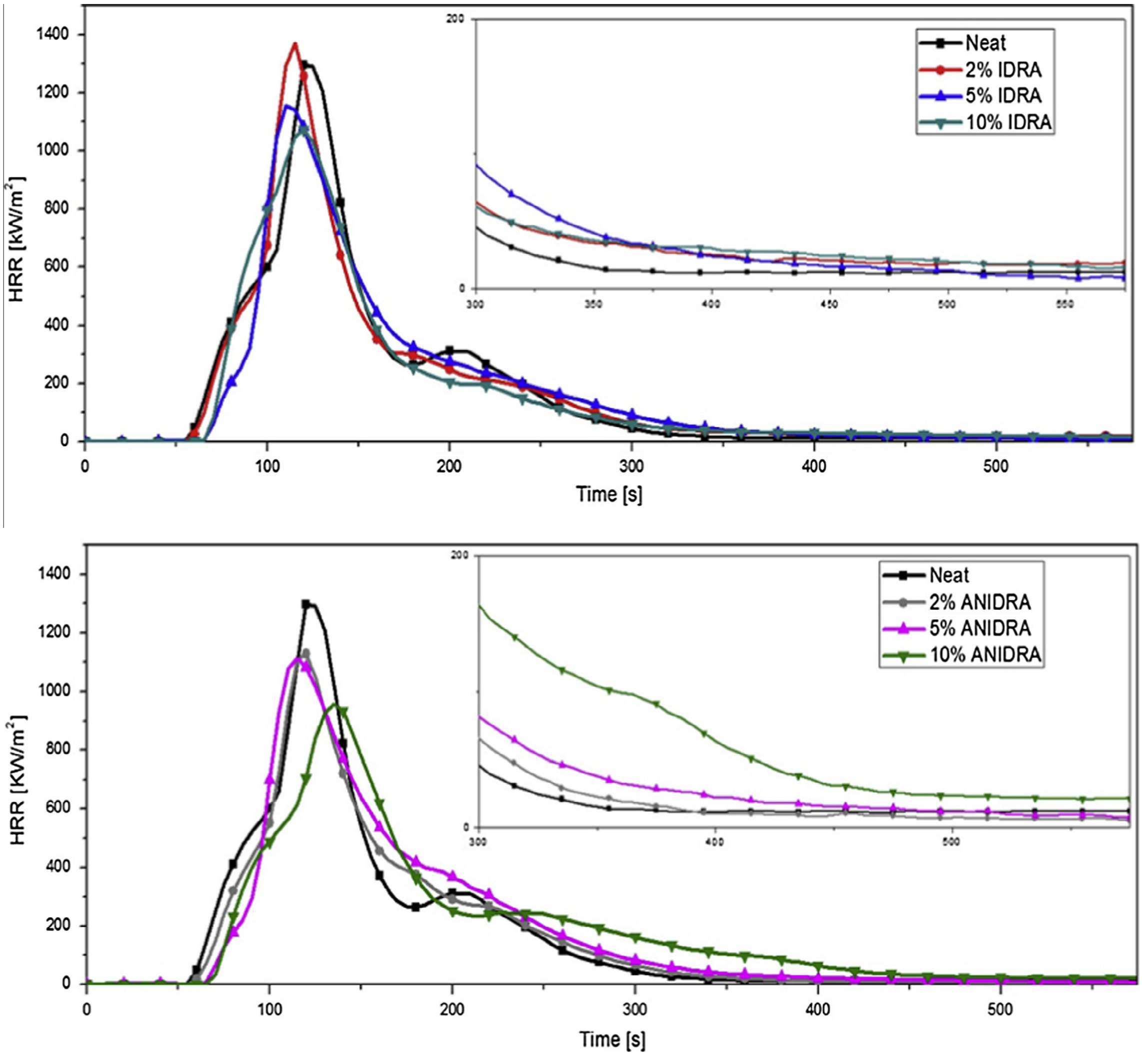

Fig. 11. Average HRR curves of the samples with hydrated sepiolite (top) and dehydrated sepiolite (bottom).

$$\left(\ln\frac{\beta}{T_{\text{peak}}^{2}}\right)=\ln\frac{AR}{E_a}-\frac{E_a}{RT_{\text{peak}}} \tag{8}$$

where T_{peak} is the temperature associated to the maximum degradation rates relative to the heating rate β, A is a pre-exponential factor, and E_a is the activation energy of the degradation step. Table 3 shows the results of Kissinger method for he examined samples.

Kissinger model reveals that the activation energies reduce with sepiolite percentage for both degradation steps; in the case of 10 wt.% filler, this variation, compared to the corresponding value for the neat resin, attain to 37% and 20%, respectively, for the two degradation steps. This effect was already shown by Liu et al. [19] studying the flame retardant mechanism of polycarbonate, containing sulphonate-silsesquioxane-fluoro. According to this work, the reduction of the activation energies results in a faster thermal degradation which promotes the formation of an insulating char layer, which could act in the direction of slowing down the whole combustion process.

3.3. Cone calorimetric results

The effect of sepiolite on fire behaviour of the hosting matrix was assessed by analysing the main parameters extracted from the cone calorimeter test results. Although the fire performance of material could not be directly related with fundamental constitutive properties such as mechanical characteristics (modulus, fracture toughness, etc.), the cone calorimeter allows the determination of indicative parameters which are generally employed to appreciate and to classify performance of material within a fire scenario.

The most important value extracted by standard cone fire tests is the HRR (heat release rate), expressed in kW/m^2. According to the ASTM E1354-04 standard test method for each specimen they must be performed three tests. Fig. 10 shows the three curves obtained for the sample with 5 wt.% of dehydrated sepiolite and its average curve.

From this curve, it can be seen that there is an initial delay period before the system releases heat, and this is because the temperature of the material is below the degradation temperature of the epoxy matrix. After that, the system releases heat as the volatiles produced during the pyrolysis start burning. The heat release reaches a maximum, identified as the peak of heat release rate (PHRR) and gradually is flattened down, due to the formation and thickening of a surface char layer. Two fundamental effects drive the evolution of HRR during the last stage of burning process, (a) separation of the flame zone from the degrading material surface, (*heat transfer*), and (b) the reduction of combustible products which feeds the fire reaction (*mass transfer*).

Fig. 11 shows the comparison between the average curves of the sample with IDRA and ANIDRA sepiolite filler. PHRR values reduce with the addition of sepiolite although the value found for 2% idra sepiolite loaded sample is slightly higher than neat epoxy. This was likely due to the averaging computation and some discrepancy of the original test results.

Comparing HRR curves in Fig. 11, it could be noticed that the samples with highest content of sepiolite (both hydrated and dehydrated) start to burn later than the other composites and hence reporting a larger flashover zone. In fact, it can be noted that the HRR of the neat sample reduces to zero after about 350 s, while for the sample with 10 wt.% of dehydrated sepiolite the curve is flattened after about 450–500 s. Fig. 12 shows the time interval within the range [40, 120] seconds in order to highlight the different TTI (time to ignition) values for the samples with different contents of sepiolite.

The residual char of a polymer can prevent the burning of combustible materials derived from the degradation and the transfer of oxygen into underlying materials; hence, char plays an important role in the flame retarding performance. Samples with the highest content of anidra sepiolite show a more coherent and dense charred residual surface which inherently act on both condensate and vapour phase to achieve a flame retardant effect. In fact, the formed compact char, especially at highest filler content, can reduce the heat flux between the flame zone and burning substrate. This will give rise to an overall delay which protects the underlying material layers from further burning and thus retarding the pyrolysis of the polymer. The HRR curves reported in Fig. 11 show a substantial reduction of the heat released rate mainly in the last part of the test, therefore extending the overall combustion period.

These effects are almost negligible for the samples filled by as-received sepiolite clay which seems to behave more similarly to the neat resin. The lasting time range of the tests, in fact, does not change substantially compared to the hosting matrix. The different effect between idra and anidra sepiolite filler, on the time period of combustion, could be reasonably related only to the presence of water which could induce morphological variation of the final charred layer during the burning process.

A further effect due to the presence of clay filler could be suitably associated to the barrier effect induced on the vapour phase. Flow of pyrolysed formed gas is reduced and prevented to reach high temperature combustion zone by the decreased permeability of the compact char. This phenomenon is related to the reduction

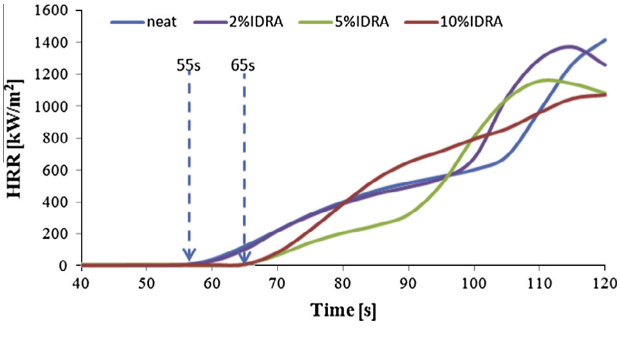

Fig. 12. Zoom-in of the HRR curves for samples loaded with hydrated sepiolite to identify TTI parameter.

Table 4
Fire behaviour of the Epon828/sepiolite samples.

Sample	PHRR (kW/m^2)	THR (MJ/m^2)	TTI (s)	FIGRA (kW/m^2 s)	Char yield (%)
Neat	1298 ± 32	97.6 ± 1.2	55	10.8	8.0
2% sep anidra	1129 ± 27	97 ± 1.9	55	9.8	8.5
2% sep idra	1370 ± 25	100.9 ± 0.3	55	11.9	8.0
5% sep anidra	1114 ± 14	106.5 ± 2.4	65	9.7	13.0
5% sep idra	1157 ± 20	99.5 ± 0.1	65	10.5	13.6
10% sep anidra	958 ± 15	107.7 ± 3.7	65	7.1	16.2
10% sep idra	1072 ± 19	95.7 ± 1.6	65	8.9	14.9

of PHRR value respectively from 1298 kW/m^2 to the 958 kW/m^2 (−26%) and 1072 kW/m^2 (−17%), respectively in the case of anidra and idra filler. It is interesting to notice that the extended time period of the combustion process does not lead to a variation of the total heat released. As showed in Fig. 13, the THR values, which correspond to the area under the HRR curves, are negligibly changed.

In principle, all char or residue formed during a fire process contribute to reduce heat and mass transfer to the flame zone by acting as a barrier layer. However, the effectiveness of the charred layer depends not only by the amount of residue but also by its morphology. In fact, permeability of the char plays a fundamental rule (a) by regulating the mass flow of combustible volatiles from the material surface to the firing zone, and (b) by varying the heat transfer either due to its thermal conductivity and its thickness. It could be concluded that the main effects of sepiolite loadings is mainly represented by a significant reduction of the PHRR level and an overall lengthen of the burning process. The testing results on the specimen with both hydrated and dehydrated sepiolite are reported in Table 4.

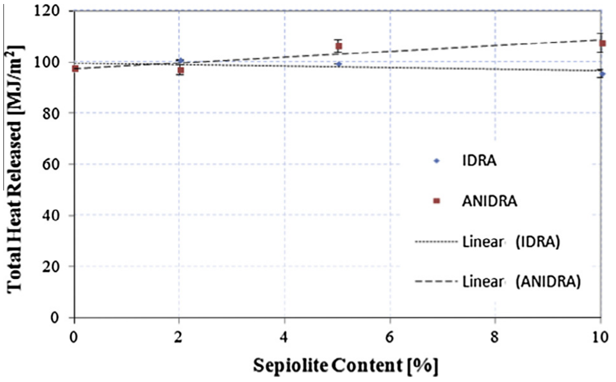

Fig. 13. THR for IDRA and ANIDRA based sepiolite samples.

From cone calorimeter tests, some interesting derived parameters could be computed. Among the others, the Fire Growth Rate Index (FIGRA) values, namely the ratio between the immediate HRR value and the time during which this value is recorded, is used to classify the fire performance of a material system. In general, this parameter is related to the burning propensity of a material [20] and it is computed according to the following relationship:

$$\mathrm{FIGRA} = \max\left[\frac{\mathrm{HRR}(t)}{t}\right] \tag{9}$$

Table 4 reports the computed FIGRA values for the performed cone calorimeter tests. The addition of sepiolite into the neat epoxy matrix, strongly reduces this parameter according to the amount by weight since the lowering of PHRR level is not coupled to a comparable increase of the occurring time (i.e. PHRRs are lower but the time in correspondence of which it occurs does not change significantly).

The visual inspection of the sample tested by cone calorimetry can give insight regarding the effect of sepiolite on consistency of the final char. Fig. 14 shows pictures of samples, both hydrated and dehydrated, before and after the cone calorimeter test. The char residue of idra sepiolite loaded samples appear more open and fractured than corresponding anidra filled system, and in particular analysing the 10 wt.% filled sample, it results that the formed char layer is characterised by a more dense and compact surface.

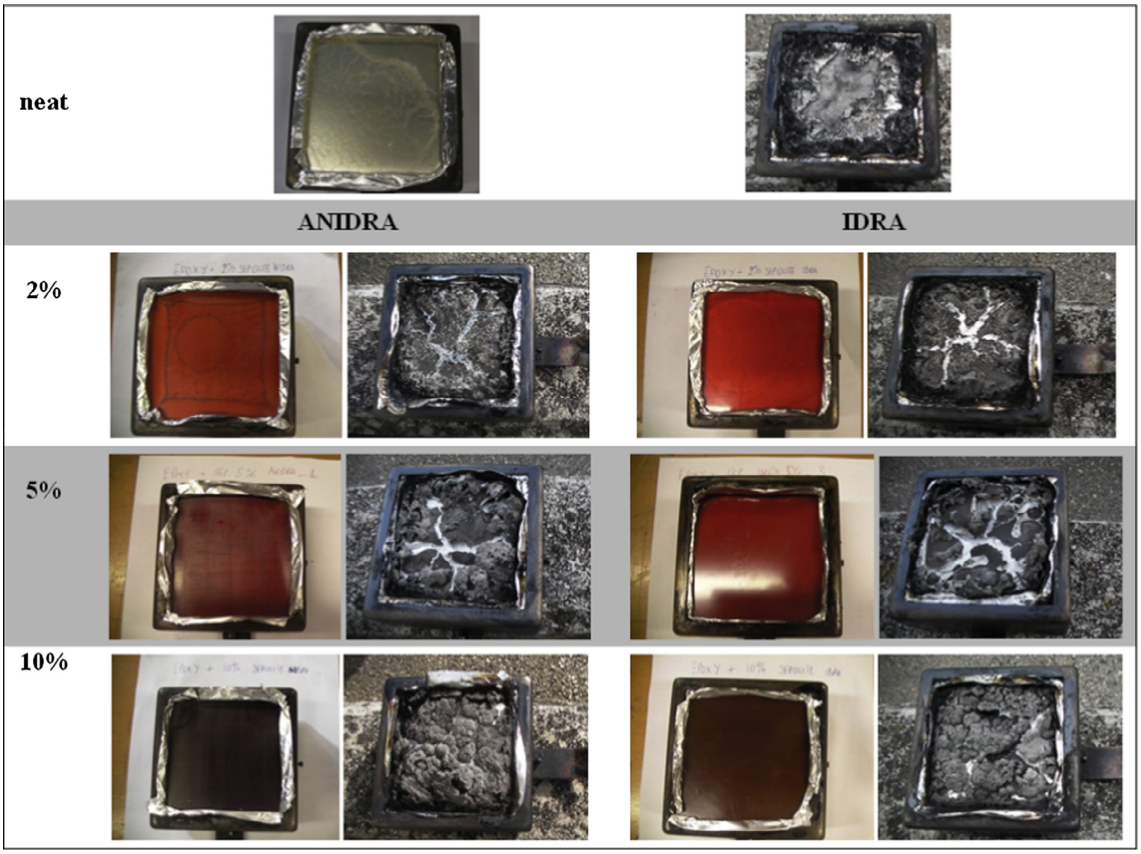

Fig. 14. Picture of the samples before and after the test.

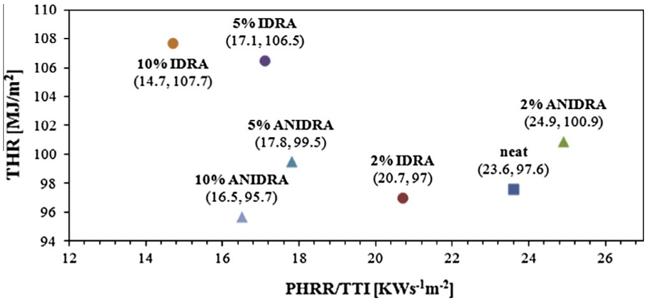

Fig. 15. Fire risk for the composites under exam.

Cone calorimetry supplies the three main parameters (THR, PHRR and TTI) to classify congruently the fire risk of different systems. In particular, fire risk could be obtained by plotting the total heat evolved against the peak of the heat release rate divided by time to ignition [21]. In such case, the *y* and *x* axis indicate respectively the propensity of the system to cause a fire of long duration and a quickly growing fire.

The results of fire risking for the experimental data obtained by cone calorimeter test performed on sepiolite loaded epoxy samples is reported in Fig. 15.

Analysis of the fire risk leads to the conclusion that high amount of dehydrated sepiolite cause a long duration but slow growing fire. On the contrary, samples containing high amount of hydrated sepiolite (10% ANIDRA) are characterised by short fire duration and a slightly reduced growing fire rate.

4. Conclusions

In this work, the influence of sepiolite clay (both hydrated and dehydrated) on the fire behaviour of an epoxy resin has been investigated. Dispersion of clay into the hosting matrix was analysed by optical and SEM microscopy. A good level of dispersion and homogeneity was found up to 10 wt.%.

Experimental results of TGA testing revealed that the effect of sepiolite, in its both used form, on the degradation behaviour of the final nanocomposite, is substantially negligible. Sepiolite acts only as inert phase during degradation of a hosting system, without any chemical interaction with the hosting matrix. Thus, effective percentage of char yield is not affected by the filler content. Analysing the peak temperatures, obtained by TGA test performed in oxidative atmosphere, the activation energies for each degradation steps were computed by using the Kissinger method. It was found a significant reduction of the first activation step energy for the samples with 10 wt.% of hydrated and dehydrated sepiolite and a lower reduction of the second step energy.

Interesting results were acquired by cone calorimetry. In fact, the addition of 10 wt.% of dehydrated sepiolite promotes a reduction of the PHRR of about 27%, from 1298 kW/m^2 to 958 kW/m^2; whereas, in the case of specimens with 10 wt.% of hydrated sepiolite the PHRR reduction is only about 17%, (i.e. 1072 kW/m^2). As the clay filler operates as an inert within the hosting system, the THR does not change significantly compared to the neat sample.

The extending of burning period and the reduction of the PHRR, in the case of idra sepiolite nanocomposite, determines a reduction of the fire risk for highest loaded samples due to the morphology of final char. Images of the specimens, before and after cone calorimetry tests, show a more and less fractured char surface, according to the sepiolite percentage compared to the neat system, especially for the anidra sepiolite based material.

In conclusion, pre-treatment of the sepiolite clay surely enhance fire behaviour of the nanocomposite compared to the as-received filler loading.

References

[1] Ellis B. Chemistry and technology of epoxy resins. London: Chapman & Hall; 1993.
[2] Pascault JP, Sautereau H, Verdu J, Williams RJJ. Thermosetting polymers. New York: Marcel Dekker; 2002.
[3] Ricciardi MR, Antonucci V, Zarrelli M, Giordano M. Fire behavior and smoke emission of phosphate–based inorganic fire-retarded polyester resin. J Fire Mater 2012;36(3):203–15. http://dx.doi.org/10.1002/fam.1101.
[4] Formicola C, De Fenzo A, Zarrelli M, Giordano M, Antonucci V. Zinc-based compounds as smoke suppressant agents for an aerospace epoxy matrix. Polym Int 2011;60(2):304–11. http://dx.doi.org/10.1002/pi.2949.
[5] Nohales A, Munoz-Espi R, Felix P, Gomez CM. Sepiolite-reinforced epoxy nanocomposites: thermal, mechanical, and morphological behavior. J Appl Polym Sci 2011;119(1):539–47. http://dx.doi.org/10.1002/app.32797.
[6] Martone A, Formicola C, Giordano M, Zarrelli M. Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites. Compos Sci Technol 2010;70(7):1154–60. http://dx.doi.org/10.1016/j.compscitech.2010.03.001.
[7] Duquesne S, Jama C, Le Bras M, Delobel R, Recourc P, Gloaguen GM. Elaboration of EVA–nanoclay systems-characterization, thermal behaviour and fire performance. Compos Sci Technol 2003;63(8):1141–8. http://dx.doi.org/10.1016/S0266-3538(03)00035-6.
[8] Samyn F, Bourbigot S, Jama C, Bellayer S. Fire retardancy of polymer clay nanocomposites: is there an influence of the nanomorphology? Polym Degrad Stab 2008;93(11):2019–24. http://dx.doi.org/10.1016/j.polymdegradstab.2008.02.013.
[9] Yu Y, Qi S, Zhan J, Wu Z, Yang X, Wu D. Polyimide/sepiolite nanocomposite films: preparation, morphology and properties. Mater Res Bull 2011;46(10):1593–9. http://dx.doi.org/10.1016/j.materresbull.2011.06.009.
[10] Suárez M, García-Romero E. Variability of the surface properties of sepiolite. Appl Clay Sci 2012;67–68:72–82. http://dx.doi.org/10.1016/j.clay.2012.06.003.
[11] Technical Data Bulletin Epon828. Houston, Momentive; 2005.
[12] Technical Data Sheet EPIKURE™ Curing Agent 3200, 3223, 3234 & 3245. Houston, Momentive; 2005.
[13] Huggett C. Estimation of rate of heat release by means of oxygen-consumption measurements. Fire Mater 1980;4(2):61–5. http://dx.doi.org/10.1002/fam.810040202.
[14] Zotti AB, Borriello A, Martone A, Antonucci V, Giordano M, Zarrelli M. Effect of sepiolite filler on mechanical behaviour of a bisphenol A-based epoxy system. Composites Part B 2014;67:400–9. http://dx.doi.org/10.1016/j.compositesb.2014.07.017.
[15] Frost RL, Ding Z. Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites. Thermochim Acta 2003;397(1–2):119–28. http://dx.doi.org/10.1016/S0040-6031(02)00228-9.
[16] Paterson-Jones JC, Percy VA, Giles RGF, Stephen AM. The thermal degradation of model compounds of amine-cured epoxide resins. II. The thermal degradation of 1,3-diphenoxypropan-2-ol and 1,3-diphenoxypropene. J Appl Polym Sci 1973;17(6):1877–87. http://dx.doi.org/10.1002/app.1973.070170620.
[17] Rose N, Le Bras M, Bourbigot S, Delobel R. Thermal oxidative degradation of epoxy resins: evaluation of their heat resistance using invariant kinetic parameters. Polym Degrad Stab 1994;45(3):387–97. http://dx.doi.org/10.1016/0141-3910(94)90209-7.
[18] Slopiecka K, Bartocci P, Fantozzi F. Thermogravimetric analysis and Kinetic study of poplar wood pyrolysis. Appl Energy 2012;97:491–7. http://dx.doi.org/10.1016/j.apenergy.2011.12.056.
[19] Liu S, Ye H, Zhou Y, He J, Jiang Z, Zhao J, et al. Study on flame-retardant mechanism of polycarbonate containing sulfonate-silsesquioxane-fluoro retardants by TGA and FTIR. Polym Degrad Stab 2006;91(8):1808–14. http://dx.doi.org/10.1016/j.polymdegradstab.2005.11.013.
[20] Kandola B, Krishnan L. Fire performance evaluation of different resins for potential application in fire resistant structural marine composites. University of Bolton, Institute for Materials Research and Innovation; 2014.
[21] Manfredi LB, Rodríguez ES, Wladyka-Przybylak M, Vázquez A. Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. Polym Degrad Stab 2006;91(2):255–61. http://dx.doi.org/10.1016/j.polymdegradstab.2005.05.003.