Kinetic Study on the Thermal Degradation of Epoxy Composites Reinforced with Non-covalent Functionalized MWCNTs

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Epoxy resin / carbon nanotubes (CNTs) nanocomposites are nowadays intensively studied in order to produce high performance materials with enhanced properties for specific applications in all activity fields, from electronics to automotive and aeronautics. In order to improve the interactions of CNTs with the polymer matrix, a functionalization of CNTs surface is often required. In this work, functionalized CNTs/epoxy nanocomposites were obtained and investigated by thermogravimetric analysis. Non-covalent functionalized CNTs with three types of surfactants were used. Activation energies of the degradation processes were calculated using Kissinger-Akahira-Sunose isoconversional method. The influence of surfactant type, functionalization mode (covalent or non-covalent) and functionalized CNTs content in composite on the activation energy as a function of the degradation conversion degree was studied.

Keywords: thermal degradation, isoconversional method, carbon nanotubes

Epoxy resins are known to have good stiffness, specific strength, dimensional stability, and chemical resistance [1-3]. The use of reinforcing agents, such as fibers or fillers aims to improve further the properties of the resulted epoxy composites and tailor them for specific applications like coatings, adhesives, electronic encapsulating compounds, automotive and aviation industry [4-5]. Carbon nanotubes (CNTs) are nowadays intensively studied as filler material to produce high performance composite structures with enhanced properties [6]. Their remarkable electronic, thermal, optical, mechanical and chemical properties, which have been attributed to the special structure of the CNTs walls [7-8], lead to numerous potential applications of CNT/polymer nanocomposites.

In order to achieve high performance nanocomposite materials, the aim should be to improve the interface adhesion between components. Thus functionalization of Multiwalled Carbon Nanotubes (MWCNT) can provide useful groups onto their surface which will interact with the polymer matrix to ensure efficient load transfer within the nanocomposite material. Through covalent functionalization one can attach a large number of functional groups. However these methods have two major drawbacks: firstly, during the functionalization reaction carried out often with strong acids, a large number of defects are inevitably created on the CNT sidewalls leading to severe degradation in mechanical properties of CNTs as well as disruption of π electron system responsible for conduction in nanotubes. Non-covalent functionalization is an alternative method for tuning the interfacial properties of nanotubes. Besides polymer wrapping, surfactants have also been employed to functionalize CNTs. Several studies have contributed to studying the effects of surfactant on dispersability and other properties of CNTs [9-10]. The surfactants studied previously include: (i) non-ionic surfactants, (ii) anionic surfactants, (iii) cationic surfactants, Surfactant adsorption through van der Waals attraction forces on the CNT surface lowers their surface tension preventing the formation of agglomerates by electrostatic/steric repulsive forces. The efficiency of this method depended strongly on the properties of surfactants [11].

The incorporation of CNTs in the epoxy polymer can enhance thermal stability (namely the glass transition temperatures, melting or thermal decomposition temperatures) as well as flame-retardant properties through their constraint effect on the polymer segments and chains [12]. Thermal properties are influenced by many factors such as CNT type, aspect ratio, dispersion within the matrix and most important the interfacial interactions with polymer matrix. The mechanisms behind this enhancement were studied by several groups [13-14] leading to two main directions: (1) the CNTs networks can act as a heat shield for the polymer below the layer, thus significantly reducing the heat release rate of nanocomposites during thermal treatment and (2) the incorporation of CNTs into a polymer leads to an enhanced thermal stability of nanocomposites, through inhibition of cracks or openings formation that could increase contact surface with high temperature environment [15].

Thermogravimetric analysis (TGA) gives information about the materials (including polymers) thermostability and the evolution of degradation process. Moreover, TGA experimental data allow some computational kinetic analysis in order to determine the activation energy of the degradation process. In this respect, isoconversional methods are used due to the advantage that they allow the computation of the activation energy independent of the reaction model.

In this work, the thermal degradation kinetics of nanocomposites obtained from epoxy resin / non-covalent functionalized carbon nanotubes were investigated by thermogravimetric analysis. The variation of activation energies as a function of degradation process conversion was calculated using isoconversional methods.

Experimental part

Materials and methods

Commercial MWCNTs supplied by Sigma-Aldrich were used (synthesized by Catalytic Chemical Vapour Deposition

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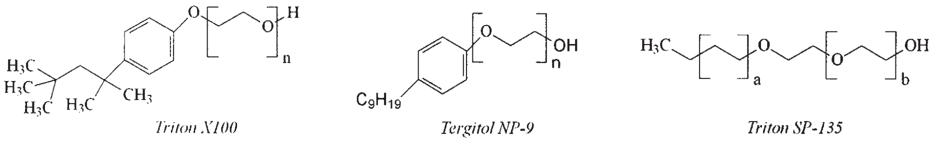

Fig. 1. Chemical structures of surfactants used for MWCNT functionalization

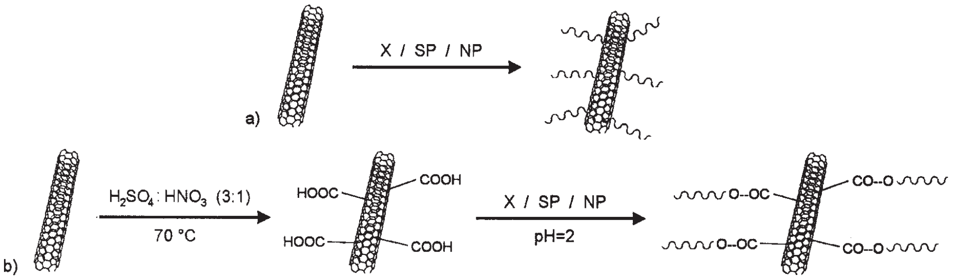

Fig. 2. Schematically representation of MWCNT functionalization a) non-covalent, b) covalent

- CCVD, with more than 90% carbon basis). The nonionic surfactants were purchased from Aldrich and used without further purification: octylphenoxypolyethoxyethanol (Triton X100), alkyl polyethylene glycol (Triton SP-135), alkylphenyl-polyethylene glycol (Tergitol NP-9). The chemical structures of surfactants are presented in figure 1. The polymer matrix used in this study was a standard diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (ER) provided by Dow Chemical, which was cured with poly(m-xylyenediamine-alt-epichlorhydrin), diamine terminated (PXDED) as the hardener supplied by Aldrich.

The non-covalent functionalization of MWCNTs was performed using three different non-ionic surfactants. Samples were prepared through physical adsorption of surfactants following the procedure described in our previous work [16] (referred as MWCNT-NP; MWCNT-X and MWCNT-SP). Alternately, pristine MWCNTs were used as reference sample. Briefly, the functionalization method consists in treating the pristine MWCNTs with a solution of surfactant in acetone under sonication. This way the individual MWCNTs are covered with surfactant molecules following by intensive washing with acetone to remove excess. For comparison, MWCNTs covalently functionalized with NP surfactant was studied. Thus, covalent linkage of surfactant was done in a two steps reaction: oxidation of MWCNTs with a strong acids mixture to create carboxyl groups on their surface, then esterification of these new groups with surfactant molecules in acid medium (as it was shown before [16]). The functionalization methods are schematically presented in figure 2. The MWCNT functionalization was proved previously by different advanced characterization methods [16].

The integration of MWCNTs into DGEBA was performed using ultrasonication tip for 2 h in order to disperse individual carbon nanotubes in a reinforcing network. Then the PXDED curing agent was added in a rate of 30.25 wt. % related to the resin and stirred manually for 2 min in an ultrasonic bath. Finally, the resin mixture was placed in a PTFE mould to form rectangular samples. The composite was then placed in an oven and maintained at 60°C for 3 h for the curing reaction to take place, and temperature was raised to 100 °C for the postcuring of residual epoxy groups

Thermogravimetric measurements of each sample were performed at four different heating rates (2, 5, 10, 20 °C/min), in nitrogen atmosphere, from ambient temperature up to 600°C, using a TGA Q500 equipment (TA Instruments). The samples weight was 2.2 ± 0.1 mg.

Isoconversional methods

The basic principle of isoconversional methods assumes that for a specific conversion degree the reaction rate depends only on the temperature.

The kinetics of a single-step reaction in solid phase is described by eq. (1):

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

where:

α is the conversion degree, t - time, T - absolute temperature, $d\alpha/dt$ - the reaction rate, $f(\alpha)$ - the reaction model, $k(T)$ - temperature-dependent rate constant. The temperature dependence of $k(T)$ obeys an Arrhenius-type expression, the e q. (1) yields:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

where:

A and E are the preexponential factors and the activation energy given by Arrhenius equation and R - the ideal gas constant.

In the case of thermogravimetrical analysis, the conversion degree α can be determined from experimental data by two ways, with similar results: directly from TGA data as a fraction of the mass loss: $\alpha = (m_o - m_t) / (m_o - m_\infty)$ (where m_0 and m_∞ are the initial and final sample weights and m_t - the sample weight at time t) or from DTG (derivative thermogravimetric) data as a fraction of the area under the DTG curve.

By logarithmation of eq. (2), Friedman [17] obtained an expression (eq. 3) that allows the computation of the activation energy:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{R}\cdot\frac{1}{T_{\alpha,i}} \tag{3}$$

This method is known as "differential isoconversional method of Friedman". The activation energy can be obtained for every value of α from the plot $\ln(d\alpha/dt)_{\alpha,i}$ vs. $1/T_{\alpha,i}$ for all the i experiments with different heating rates β_i. This method has the advantage to be free of approximations and it is not limited to constant heating rates β_i (not necessary a linear variation of temperatures) [18]. Unfortunately, the Friedman method leads to unstable activation energy values in the case of noisy experimental data due to numerical differentiation and may conduct to systematic errors when the reaction heat significantly changes with the heating rate [19]. This problem could be avoided by using integral isoconversional methods [18].

Usually, experimental data series with constant heating rates $\beta_i=dT/dt$ are used in order to apply isoconversional methods. Thus, eq. (2) can be written:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (4)$$

and by integration:

$$g(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^{T_\alpha}\exp\left(-\frac{E}{RT}\right)dT \qquad (5)$$

The right side integral of eq. (5) can not be analytically solved, thus the equation can be rewritten as:

$$g(\alpha)=\frac{AE}{\beta R}\left[\frac{\exp(-x)}{x}-\int_x^{\infty}\frac{\exp(-x)}{x}dx\right]=\frac{AE}{\beta R}\cdot p(x) \qquad (6)$$

where $x=E/RT$. Even in the new form, the integral from eq. (6) does not exhibit an analytical solution, but the function $p(x)$ can be estimated using different approximations.

One of most used method was proposed by [20, 21], using the approximation $p(x)=e^{-x}/x^2$. They obtained eq. (7) (KAS method):

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)=\ln\left(\frac{AR}{E_\alpha}\right)-\ln[g(\alpha)]-\frac{E_\alpha}{RT_{\alpha,i}}=const.-\frac{E_\alpha}{R}\cdot\frac{1}{T_{\alpha,i}} \qquad (7)$$

The activation energy is determined from the plot of left side of eqs. (7) versus $1/T_{\alpha,i}$ at constant conversion degree α, for the *i* heating rates.

Other methods were developed by [22, 23] respectively by [25] using [24] approximation (OFW method). The OFW method leads to less accurate result than KAS method and it was improved by Sbirrazzuoli et al. [26].

Opposite to these early methods which use approximation, an integral method using numerical integration was proposed recently [27, 28], increasing the accuracy of determined activation energy (known as non-linear isoconversional method - NLN). This method takes into account a possible variation of the activation energy.

In this work only KAS method was used for kinetic study. This method was recently recommended by ICTAC Kinetics Committee for good accuracy (from integral methods which use approximation) [29].

Results and discussions

Thermal decomposition study

The TGA and DTG curves for the epoxy nanocomposites using as reinforcing agent raw MWCNTs, respectively 3 types of non-covalent functionalized MWCNTs (with 0.6 wt. % nanofiller content) are comparatively presented in figure 3, at 10 °C/min heating rate.

In all cases, a small mass loss can be observed with a maximum degradation rate at about 150°C. This degradation can be considered finished at 250°C (both TGA and DTG curves show a plateau zone around this temperature) and the mass loss corresponding to this process was estimated at 250°C (Δm_{250}). The values of mass loss vary from 1 to 1.4 %, depending of the MWCNT chemical modification (table 1). A possible explanation could be the degradation of labile C-N bonds from the remaining amine molecules, caused by the fact that the epoxy groups do not reach full conversion even after postcuring reaction. Excess amine molecules could segregate from the polymer network to the surface and will degrade at lower temperatures than the epoxy nanocomposites.

Although in the TGA curves (fig. 3) the main degradation process of ER / MWCNTs composites seem to be single step degradation, the DTG curves show a lateral shoulder that confirm the presence of minimum 2 parallel processes.

Due to minor differences between samples in TGA/DTG curves, this point forward the influence of different parameters on the composite thermostability will be presented in tables.

The characteristic temperatures of the degradation process are presented in table 1. These temperatures correspond to start of the degradation (T_i), onset on TGA curves (T_{onset}), 5% mass loss ($T_{5\%}$) and maximum degradation rate (*Tmax*). The thermostability of ER / MWCNTs composites increases when functionalized MWCNTs were used, due to a better dispersion in ER matrix. Even through the degradation process starts about 10 °C higher (T_i) when SP or X surfactants are used, for all other

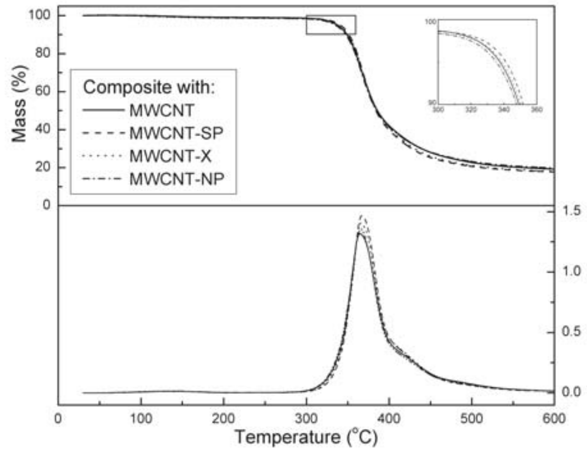

Fig. 3. TGA curves for epoxy/MWCNTs nanocomposites, with 0.6 wt. % nanofiller content (raw and non-covalent functionalized MWCNT) at 10 °C/min heating rate

Table 1
SIGNIFICANT TEMPERATURES FOR THE DEGRADATION PROCESS AND RESIDUAL MASS (AT 600 °C) FOR ALL ER / MWCNTs COMPOSITES

Nanofiller in composite	Δm_{250} %	T_i °C	T_{onset} °C	$T_{5\%}$ °C	T_{max} °C	m_{resid} %
MWCNT	1.01	287.8	345.9	337.6	365.1	19.23
MWCNT-SP	1.14	298.3	348.9	341.2	367.1	17.75
MWCNT-X	1.35	298.8	348.3	338.7	366.2	18.05
MWCNT-NP	1.28	291.5	346.0	335.4	366.1	19.79

Table 2
MAIN TEMPERATURES FOR THE DEGRADATION PROCESS AND RESIDUAL MASS (AT 600 °C) FOR COMPOSITES WITH NON-COVALENT / COVALENT FUNCTIONALIZED MWCNT, AT 10 °C/MIN HEATING RATE

Nanofiller in composite	T_i °C	T_{onset} °C	$T_{5\%}$ °C	T_{max} °C	m_{resid} %
MWCNT	287.8	345.9	337.6	365.1	19.23
MWCNT-NP	291.5	346.0	335.4	366.1	19.79
MWCNT-COO-NP	295.8	349.1	341.2	365.7	18.57

Table 3
MAIN TEMPERATURES FOR THE DEGRADATION PROCESS AND RESIDUAL MASS (AT 600 °C) FOR ER / MWCNT-X COMPOSITES WITH 0.3, 0.6 AND 1 WT. % NANOFILLER, AT 10 °C/MIN HEATING RATE

Nanofiller in composite	T_i °C	T_{onset} °C	$T_{5\%}$ °C	T_{max} °C	m_{resid} %
MWCNT-X 0% (ER / PXDED)*⁾	-	347.8	337.9	-	-
MWCNT-X 0.3%	298.2	348.7	338.9	366.5	17.96
MWCNT-X 0.6%	298.8	348.3	338.7	366.2	18.05
MWCNT-X 1%	299.3	349.6	340.5	372.4	17.64

*⁾ values from a previous work [16]

temperatures the differences are limited at maximum 3 °C. Simultaneous with T_{max}, an increasing of the maximum degradation rate can be observed on DTG curves in the case of functionalized MWCNTs. It is interesting to remark that the ER / MWCNT-SP composites have the higher thermostability, whilst the composites with MWCNT-NP show similar thermostability as those with raw MWCNTs (due to different chemical structures of surfactants and their interactions with MWCNT). The residual mass (at 600 °C) decreases with the incresing molecular weight of surfactant, with a minimum for MWCNT-SP.

The influence of MWCNT surface modification method (covalent or non-covalent) on the composite thermostability was studied using the same functionalization agent (Tergitol-NP, due the fact that ER / MWCNT-NP composite does not present a thermostability increase). In both cases, 0.6 wt. % of functionalized MWCNTs was used for obtaining the nanocomposites. The main temperatures corresponding at 10 °C/min heating rate are presented in table 2. An increasing of thermostability for the composite with covalent modified MWCNTs can be observed (by 3-5 °C). In this case the surfactant molecules are chemically attached (strongly) to MWCNT surface and not only by adsorption on the surface (physical attraction). Moreover, the presence of covalent bond between MWCNT and (some) surfactant molecules does not exclude the possibility that another surfactant molecules attach non-covalently on the MWCNT. Thus, functionalized MWCNTs have a higher compatibility and a better dispersability in the epoxy matrix.

The influence of non-covalent functionalized MWCNTs amount in composite on the thermostability was also studied, using MWCNT-X in 0.3, 0.6 and 1 wt. % ratio. In all cases the thermostability was higher than the simple cured polymer matrix (ER/PXDED) [16]. The main temperatures (table 3) are similar for 0.3 or 0.6 wt. % MWCNT-X in nanocomposite, but lower than the case with 1%.

Isoconversional decomposition kinetics

In order to use isoconversional methods to calculate the activation energy E_α as a function of the conversion degree of the degradation process α, four thermogravimetric measurements at different heating rates (2, 5, 10, 20 °C/min) were performed for each composite material. Figure 4 shows the TGA/DTG curves for all heating rates, for the ER / MWCNT-NP composite (0.6 wt. % nanofiller content). As it was expected, for all samples the curves are translated to higher temperatures with the increase of the heating rate, due to thermal inertia (doubling the heating rate conduct to an approximately 15 °C shift) [29].

KAS integral isoconversional method was used. The degradation process conversion α was calculated from DTG data as fraction of the area under the DTG curve.

The typical plot for KAS isoconversional method consist in representations of $ln(\beta/T^2)$ vs. $1/T$ (eq. 7) at different extent of degradation α. In the case of perfect experimental data (or theoretically calculated data) the points corresponding to the same conversion α for all heating rates β are collinear. The activation energy E_α for each α is determined from the slope of these lines. Good linearity of points was observed for all the samples (example in fig. 5

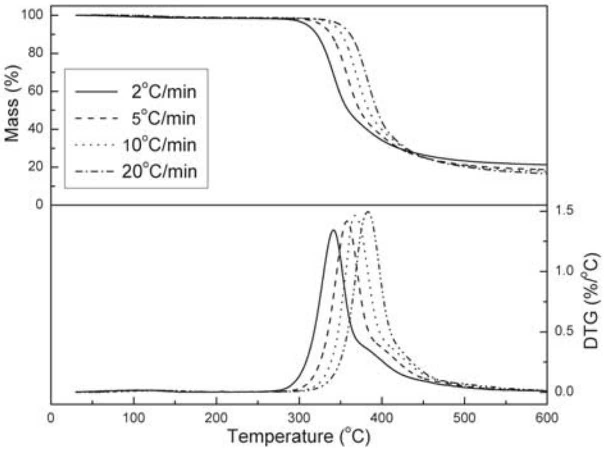

Fig. 4. TGA and DTG curves for ER / MWCNT-NP composite (0.6 wt. % nanofiller content) at different heating rates

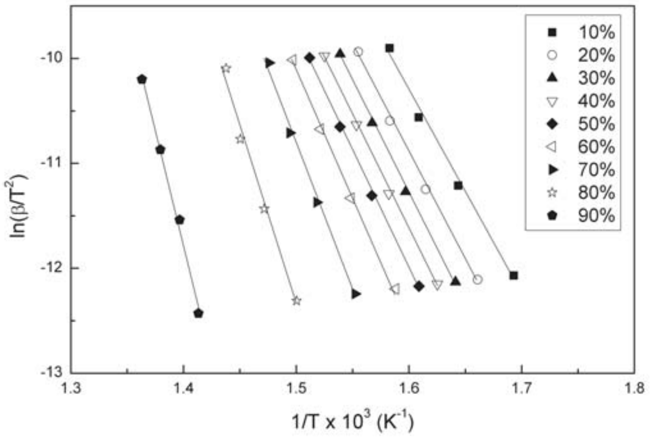

Fig. 5. Plot of *ln*(β/T^2) vs. *1/T* according to KAS method, at different extents of degradation for the ER / MWCNT-NP composite, with 0.6 wt. % nanofiller content

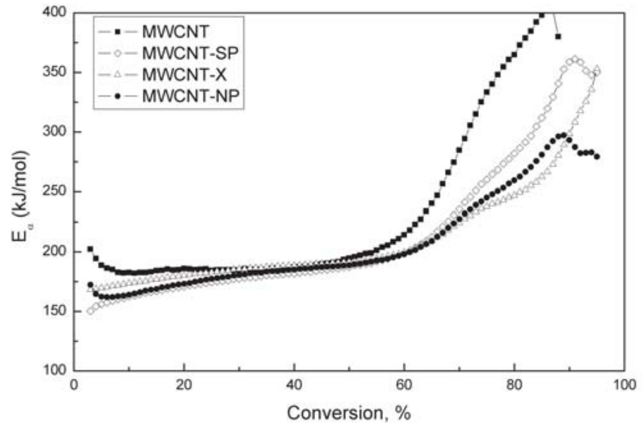

Fig. 6. Activation energy E_α as a function of degradation conversion for epoxy nanocomposites using raw and non-covalent functionalized MWCNT

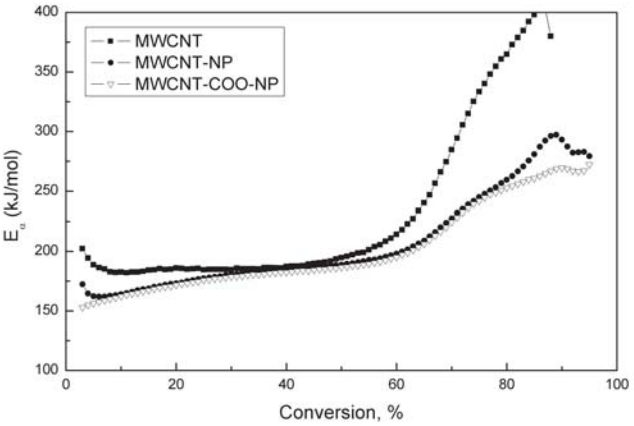

Fig. 7. Activation energy E_α as a function of degradation conversion for epoxy nanocomposites with covalent and non-covalent functionalized MWCNTs

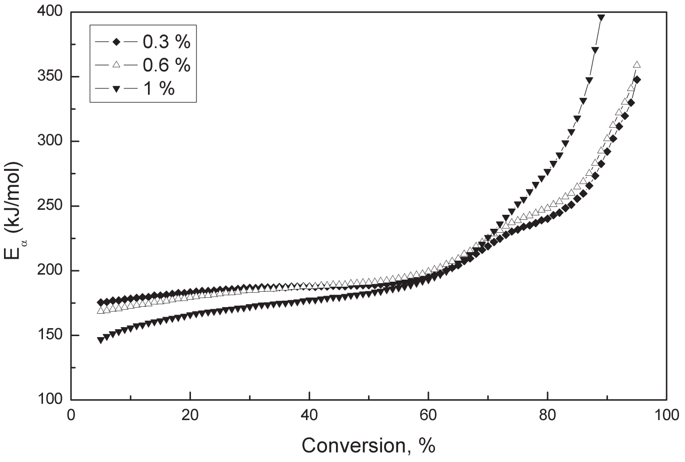

Fig. 8. Activation energy E_α as a function of degradation conversion for ER / MWCNT-X composites with 0.3, 0.6 and 1 wt. % nanofiller

for the ER / MWCNT-NP composite, with 0.6 wt. % nanofiller content).

The evolution of activation energy E_α as a function of degradation conversion for epoxy nanocomposites using raw and non-covalent functionalized MWCNT (fig. 6) shows two distinct zones for all samples, confirming a degradation process in (minimum) two steps. The first zone, until a conversion degree of about 50 % is characterized by a quasi-constant value of activation energy (especially in the case of composites with raw MWCNT). Even a small variation of E_α (less than 15% between minimum and maximum value) is accepted in order to consider that zone to be a "single step" process [29]. The values of E_α for conversion interval 30-50% are similar for all the samples (about 180±5 kJ/mol), this zone corresponding to the degradation of the polymer matrix.

In the second zone, an important increase of E_α can be observed. This zone can be assigned to the degradation of molecules attached to the MWCNT (surfactants), which occurs at 300-500 °C [16]. Due to different chemical structure of functionalization agents, the E_α values for the second zone vary significantly from a composite sample to another, with the highest values in the case of composite with unfunctionalized MWCNTs (higher thermostability). It is important to remark that the degradation of functionalized MWCNTs starts at about 300 °C [16], thus in the first zone this process superposes with the degradation of the epoxy matrix. This fact explains the slow increase of E_a values for the first zone in the case of composites with functionalized MWCNTs.

The type of MWCNTs functionalization, covalent or non-covalent, with the same surfactant seems to have not an influence on the E_a values (fig. 7). Differences appear only for a degradation extent higher than 80%, where the E_a of composite ER / non-covalent functionalized MWCNTs is higher (the –COO– groups in the case of covalent functionalization lead to an easier degradation).

The variation of activation energy E_α as a function of degradation conversion for ER / MWCNT-X composites with different content of carbon nanotubes (0.3, 0.6 and 1 wt. %) is presented in figure 8. Similar values and evolution of E_a are observed in the cases of 0.3 and 0.6 % MWCNT content in composites (in accordance with similar values for the main temperatures of degradation process previously presented in table 3).

Conclusions

The thermal degradation of functionalized MWCNTs / epoxy nanocomposites was investigated by thermo-gravimetric analysis. Non-covalent functionalized MWCNTs with three types of surfactants were used. For all composites, the global degradation process occurs in two steps, the limit between the two zones is at a conversion value of about 55%. The first zone is assigned to the degradation of epoxy matrix and the second to the functionalization agent, but the two processes occur in parallel for a period. The use of functionalized MWCNTs leads to an improvement of composite thermostability than the case of raw MWCNTs/epoxy composite, but the difference is of maximum 5°C (for 0.6 wt.% CNTs in composite), depending on the type of surfactant. Covalent functionalized MWCNTs composites show a higher thermostability than the case when non-covalent functionalized MWCNTs are used. The thermostability of composites increases with functionalized MWCNTs content, with higher values at 1 wt.%, but significant differences were not observed between 0.3 and 0.6 wt.% CNTs. The activation energies E_α of composites degradation processes were calculated using Kissinger-Akahira-Sunose isoconversional method. The two zones of degradation process are confirmed by the evolution of E_α values as a function of degradation conversion. In the first zone, the values of E_α are similar, but the differences are significant for the second zone, where the type of functionalization agent has a significant role in the degradation process of functionalized MWCNTs

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