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THERMAL DEGRADATION AND FIRE PROPERTIES OF EPOXY MODIFIED RESINS

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The flammability of the resin is a major limitation in the aeronautic applications where new developed materials for primary and secondary structures must fulfill special regulation in order to demonstrate that their level of fire safety is equivalent to a conventional transport (aluminum) material. In this paper, the attention is focused on the thermal properties and the fire behavior of TGMDA based epoxy resins in which carbon nanotubes and POSS have been dispersed at nanometric or molecular level. The effect of the hardener, the diluent and the nanoparticles on the thermal properties has been investigated. Thermogravimetric data have been modeled according to the Coats and Redfen equations which provide a fast method for the determination of the kinetics of thermal degradation of polymers. The char yield has been used as criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftyzer equation and the results have been compared with the experimental LOI data

Introduction

Advanced composite materials are becoming more important in the construction of aerospace structures. Their use allows to the designers a large field of action that was not possible with traditional materials1, 2. Nanotechnology offers in composite materials the possibility to impart multifunctionality3-5, and durability6 in a single load bearing materials. Between the different functions that can be imparted though the nanotechnology strategy flame resistance is still a big challenge7. There are several possible ways to chemically modify a thermosetting epoxy resin in the direction to reduce their flammability. The addition in epoxy resins of little concentration of Polyhedral oligomeric silsesquioxane compounds (POSS) is recognized to be a successful method to reduce their flammability 7,8. The evaluation of the fire properties of a material studied at laboratory level it is not a simple feasibility. The majority of the available techniques are destructive using big amounts of precious sample. Moreover, fire laboratory equipment is hazardous and requires particular safety procedures. The possibility to provide models, where results obtained using laboratory scale equipment (such as the thermogravimetric techniques) are related fire testing experiments, offers the advantages to allow the evaluation of the fire properties without wasting precious material.
In this paper, the attention is focused on the thermal properties and the fire behavior of 4,4'-methylenebis(N,N-diglycidylaniline) (TGMDA) based epoxy resins in which carbon nanotubes and POSS have been dispersed at nanometric or molecular level. The effects of the hardener, the diluent and the nanoparticles on the thermal properties have been investigated. Thermogravimetric data have been modeled according to the Coats and Redfen equations9 which provide a fast method for the determination of the kinetics of thermal degradation of polymer. The char yield in the range of temperature between 700 and 800°C, has been used as criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftyzer equation10 and the results have been compared with the experimental LOI data.

Materials and methods

Materials: 4,4'-Methylenebis(N,N-diglycidylaniline)(TGMDA), 1,4-butanedioldiglycidyl ether (BDE) and 4-aminophenil sulfone (DDS) were purchased form Aldrich. MWCNts (grade 3100) from Nanocyl, and three different POSS compounds: Glycidyl POSS Cage (GPOSS) and Epoxycyclohexyl POSS (ECPOSS) functionalized with epoxy containining groups and DodecaPhenyl POSS (DPHPOSS) functionalized with phenyl groups.POSS were purchased from Hybrid Plastics. All analyzed formulations are listed in table 1.

TABLE 1. Samples and formulations

Sample	Nanofiller type	Nanofiller wt%	Sample	Nanofiller type	Nanofiller wt%
T20BD			T20BD 0.5 CNT	MWCNT	0.5
T20BD DPH POSS	DPH POSS	0.5	T20BD DPH POSS 0.5 CNT	DPH POSS MWCNT	0.5 0.5
T20BD EC POSS	EC POSS	0.5	T20BD EC POSS 0.5 CNT	EC POSS MWCNT	0.5 0.5
T20BD G POSS	G POSS	0.5	T20BD G POSS 0.5 CNT	G POSS MWCNT	0.5 0.5

Samples were obtained according to procedure already described in the work made by Raimondo et al. The epoxy matrix was obtained by mixing at 80-90°C TGMDA with BDE monomer at a ratio of concentration epoxide to diluent of 80%: 20% (by wt). Subsequently the hardener was added at 120°C under mechanical stirring until complete dissolution. The misture was purred into the stainless steel mold and cured by a two-stage curing cycles: a first isothermal stage at the lower temperature of 125 °C for 1 hour and the second isothermal stage at 200 °C for 3 hours. The hardner DDS was added at a stoichiometric concentration with respect to all epoxy rings (TGMDA, BDE and POSS – in the case of POSS with epoxy rings). Sample containing MWCNT have been prepared by dispersing for 20 minutes the Carbon nanotubes in the epoxy resin before the addition of the diluent. A Hielscher model UP200S-24 KHZ high power ultrasonication probe was used for the purpose. The POSS compounds were dispersed in the epoxy matrix before the addition of the hardener. Thermogravimetric analysis (TGA) was carried out in nitrogen using a Mettler TGA/SDTA 851 thermal analyzer. Temperature range was 25-900 °C at a heating rate of 10 °C/min. Oxigen index was measured according to ASTM 2863 method.

Results and discussion

Thermogravimetric curves of the analyzed samples are shown in Figure 1.
The char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftyzer10 equation in our case we consider the value of the char yield at 700 and 800°C

$$LOI = 17.5 + 0.4Y_c$$

Where Yc is the char yield at the opportune temperature. LOI values of different blends calculated on their chair yield are shown in Table 2. In the same table the obtained values are also compared with the experimental data obtained with the ASTM 2863.

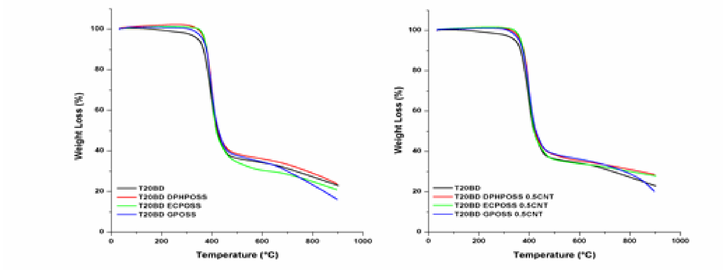

FIGURE 1. Thermogravimetric curves for all analyzed samples.

Results shown in Table 2 demonstrate a good agreement between the experimental and calculated data.

TABLE 2. Experimental and calculated LOI indexes.

Sample	700°C Yc %	Calculated LOI @700°C %	800°C Yc %	Calculated LOI @800°C %	EXPERIM LOI ASTM 2863 %
T20BD	23	29	20,5	26	27
T20BD 0.5 CNT	15	30	23,1	27	28
T20BD DPH POSS	24	31	29	29	30
T20BD EC POSS	21	29	25	27,5	28
T20BD G POSS	16	29,5	23,3	27	33
T20BD DPH POSS 0.5 CNT	29	31	31,1	30	31
T20BD Ec POSS 0.5 CNT	28	30	30	29,5	29
T20BD G POSS 0.5 CNT	20	31	28,9	29	30

TGA is also studied to determine the thermal degradation kinetics of polymers. The statistical analysis of the degradation behavior was studied by integral method of Coats and Redfern model.
This method, as reviewed by Johnson and Gallagher is an integral method that assumes various orders of reaction and compares the linearity in each case to select the correct order. The equations are given below:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \qquad \text{for } n \neq 1$$

$$\log\left[\frac{-Log(1-\alpha)}{T^2}\right] = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \qquad \text{for } n = 1$$

By plotting the appropriate left-hand side of the below equations versus 1/T, the slope equals to E/2.303R; E, which is the activation energy for the decomposition, can be calculated from these equations.
This method has been applied to our thermogravimetric data. A linear regression has provided the best fit value of n, where n was taken as 0, 0.5, 0.67, 1 and 2. The degradation kinetics was analysed by using the above order of reaction for different blends in the range of 10 and 65% weight loss of the TGA curves. The results revealed that the degradation follows first order of reaction (n=1) with correlation coefficients as indicated in table 3.3.
Figure 2 shows this plot for the sample 20BD and for sample T20BDECPOSS0.5CNT.
The activation Energy (E) were calculated using the above equation E=-2.303R/Slope and data are summarized in Table 5.

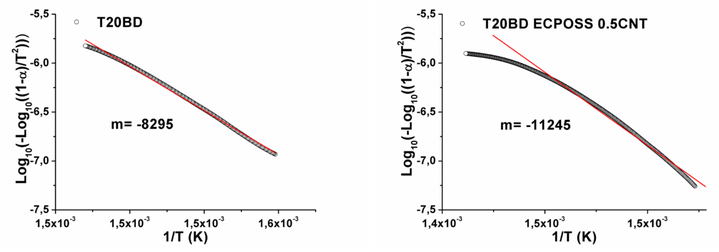

FIGURE 2. Coats and Redfern plot for sample T20BD and for sample T20BDECPOSS0.5CNT.

Values in Ea highlight that all the analysed POSS compounds slow down the degradation kinetic. The most relevant effect is detected for EC POSS. In addition, where POSS and CNT were embedded inside the epoxy matrix, the negative effect of CNTs in the degradation kinetic is compensated by the presence the POSS. In fact, formulation T20BD 0.5 CNT is characterized by a value of Ea equal to 121 kJ/mol , whereas the energy of activation for samples T20BD DPH POSS 0.5 CNT; T20BD EC POSS 0.5 CNT and T20BD G POSS 0.5 CNT ranges between 167 and 215 kJ/mol. The increase in these last values evidences the very positive effect of the POSS also in the formulations nanofilled with MWCNTs.

TABLE 4. slope and R2 squared-correlation coefficients for Coats and Redfern plots and activation energy for all the analyzed samples

Sample	m	R^2	Ea (kJ/mol)	Sample	m	R^2	Ea (kJ/mol)
T20BD	-8295	0.9825	159	T20BD 0.5 CNT	-6333,4	0.9676	121
T20BD DPH POSS	-10319	0.9873	198	T20BD DPH POSS 0.5 CNT	-9987,3	0.9981	191
T20BD EC POSS	-10504	0.9948	201	T20BD EC POSS 0.5 CNT	-11245	0.9951	215
T20BD G POSS	-9318	0.9730	178	T20BD G POSS 0.5 CNT	-8716,8	0.9996	167

Conclusions

In this paper the effect of the hardener, the diluent and the nanoparticles on the thermal properties of the TGMDA epoxy resin has been investigated. TGA analysis of cured system were used to determine the char yield and to calculate LOI index using the Van Krevelen and Hoftyzer equation. Char yields were considered both at 700°C and 800°C and LOI was calculated at these two temperatures. There was a good agreement between experimental and calculated data in either case. TGA was also studied to determine the thermal degradation kinetics of polymers using the Coats and Redfern model. The Activation energy for the thermal degradation was calculated for the different samples. The obtained results are promising for the application of the analysed materials in the aeronautic field. In fact another drawback of composite material is related to the insulating properties of the resins used to manufacture CFR composites. A very useful strategy to increase the electrical conductivity of aeronautic resins is the incorporation of conductive nanofiller inside the epoxy formulation[13, 14]. As shown in this paper the incorporation of CNT in the epoxy resin causes a negative effect on the degradation kinetics. The addition of little amounts of POSS compounds allows the use of CNTs without increasing the kinetic degradation.

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