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Effects of novel reactive toughening agent on thermal stability of epoxy resin

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Abstract A reactive amino-ended toughener was blended with different commercial epoxy resins namely, diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol F, diglycidyl *p*-aminophenol and 1,5-naphthalenediamine as curing agent. The toughener was an aromatic amino-ended copolyethersulphone (coPES):poly(ether-sulphone)–poly(etherether-sulphone). The effect of the toughener on the thermal decomposition and char oxidation behaviour of the epoxy resins was studied by the simultaneous differential thermal analysis and thermogravimetric techniques. The glass transition temperature (T_g) as well as characteristic parameters of decomposition, initial decomposition temperature (T_i) and temperature at maximum degradation rate (T_m), in both inert and oxidative environments, were determined in order to verify the influence of toughener on the thermal degradation of the different epoxy systems. It was observed that the presence of coPES maintains the high level thermal stability of the resin and that the glass transition temperature increase with the toughener percentage.

Keywords Epoxy resin · Toughener · Thermal stability · DTA–TG · Copolyethersulphone

Introduction

Epoxy resins are an important class of polymeric materials, characterised by the presence of more than one three-membered ring known as the epoxy ("epoxy" is derived from the Greek prefix "ep," which means over and between, and "oxy," the combining form of oxygen), epoxide, oxirane, or ethoxyline group [1]. By strict definition, epoxy resins refer only to uncross-linked monomers or oligomers containing epoxy groups. However, in practice, the term "epoxy resins" is loosely used to include cured epoxy systems [2]. It should be noted that very high molecular weight epoxy resins and cured epoxy resins contain very little or no epoxide groups. The vast majority of industrially important epoxy resins are bi- or multifunctional epoxides: the monofunctional epoxides are primarily used as reactive diluents, viscosity modifiers, or adhesion promoters systems [2]. Epoxies are one of the most versatile classes of polymers with different applications such as metal can coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives and aerospace composites. Therefore based on their commercial applications, they can be categorised for non-structural or low-temperature applications and structural or high-temperature applications [3]. One of the most important structural applications of epoxy resins is as matrix for structural adhesives and composites for aerospace [1, 4]. The liquid resin is cured, to provide thermoset characteristics, by a polycondensation reaction, which involves the opening of the three membered epoxide ring by reaction with catalysts or curing agents giving rise, however, to a very brittle-cured resin systems [5]. The toughness of the resin can be improved by using additives (tougheners), which lower the rate of curing [6] and can also become cross-linked due to their reactive end groups [6, 7] resulting in a tougher cured network [8]. In some cases, the modified cross-link density of the network structure enhances the toughness and decreases ductility and brittleness of the resin [9, 10].

Aromatic thermoplastic poly(ether-sulphone)s (PESs) can be used as toughening agents of epoxy resins [11–14]

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with an advantage over traditional tougheners (i.e. rubbers) owing to the resulting thermoplastic/thermoset blends do not show decrement of mechanical and thermal properties if compared with unmodified resin. In addition, if reactive PESs are used as modifiers, interpenetrating networks (IPNs) can be formed, so giving rise to blends showing enhanced mechanical and thermal properties [15]. Since in the past, some miscibility problems were encountered by using high molecular mass PESs for the purpose as toughening agents [16, 17], low molecular mass PES copolymers have been considered for this use [16, 18–20]. Many polymers containing ether, ketone and sulphone groups have been synthesised in our laboratory that can have potential application as toughening agents [19–27]. These polymers show usually good thermal and mechanical properties, and it has been reported in literature that a wide spectrum of characteristics can be obtained by balancing opportunely various groups [11].

Poly(ether-sulphone)–poly(etherether-sulphone) (PES–PEES) copolymers, whose chains are more flexible than PES because of the presence of a larger number of ether links, present a good balance between low viscosity, high glass transition temperature (T_g) and thermal stability. We thus investigated in the past low molar mass Cl–, NH_2–, OH– and COO^-– ended PES–PEES copolymers, at various PES–PEES ratios, in order to compare their comprehensive thermal stabilities and rheological properties [19, 20, 26]. Both thermal and rheological parameters were widely dependent on copolymer composition in every case, but the trends observed for the various series of copolymers were different from each other. On the basis of the comprehensive picture of the results in Refs. [19, 20, 26], the 40:60 PES–PEES amino-ended copolymer appeared to us as the most suitable for use as toughener because its thermal and rheological parameters reasonably average among the needs of various uses.

The aim of this work was to investigate the effect of 40:60 PES–PEES on the properties of several epoxy blends cured by 1,5-naphthalenediamine (ND). We determined here the glass transition temperature, as well as characteristic parameters of decomposition, initial decomposition temperature (T_i) and temperature at maximum degradation rate (T_m) in both inert and oxidative environments, of all the blends. The total contents of toughener were varied, one set contained a total 10% and the other 20 and 30%, respectively, of the thermoplastic copolymers.

Experimental

Materials

The epoxy resin were: diglycidyl ether of bisphenol A (DGEBA) supplied by Shell Chemical, Akron (USA); diglycidyl ether of bisphenol F (DGEBF) supplied by Huntsman Advanced Materials, Basel (Switzerland); triglycidil *p*-aminophenol (TGAP) supplied by Huntsman Advanced Materials, Basel (Switzerland). The curing agent was ND supplied by Sigma Aldrich, Milan, Italy. The thermoplastic polymer was an amino-ended copolyethersulphone (coPES), 40:60 PES–PEES prepared in our laboratories with a molecular weight (M_n) of 9000 ± 500 g mol^{-1}. The details on the synthesis of coPES and their characterisation are reported elsewhere [18]. The structures of all reagents are reported in Table 1.

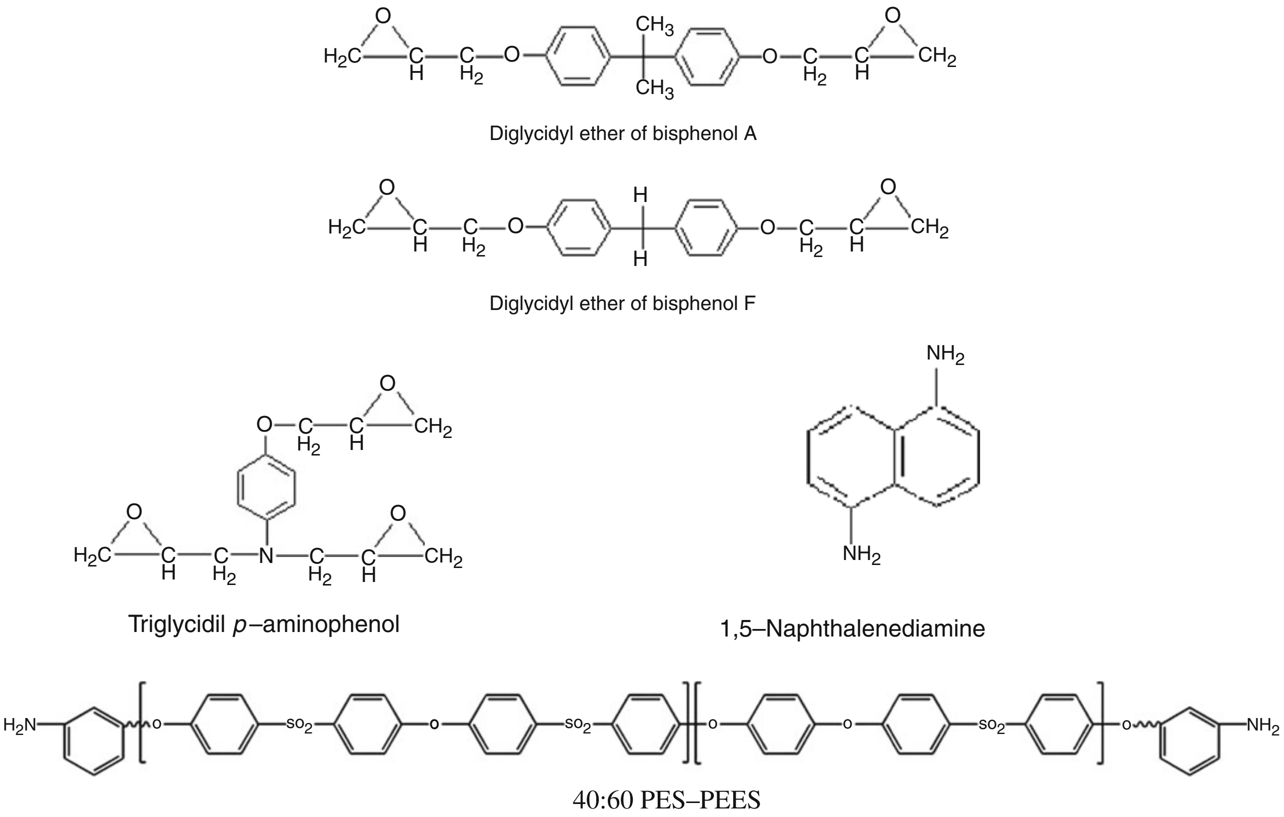
The formulations were prepared mixing the coPES and the epoxy monomer at 120 °C for 2 h. When the solution was homogeneous and the thermoplastic thoroughly dissolved in the resin the blend's temperature was lowered to 80 °C. The curing agent was then added and the resulting blend mixed for 1 h. The cured samples were prepared pouring the uncured blends in a preheated mould and degassed for 30 min at 125 °C. The temperature was then increased at 2 °C min^{-1} to 180 °C and hold at this temperature for 3 h. At the end of this curing cycle, the panels were allowed to cool slowly at room temperature.

Thermal analysis

A Shimadzu DTG-60 simultaneous DTA–TG apparatus was used for both thermogravimetric analysis (TG) and differential thermal analysis (DTA). The calibrations of temperature, heat flow and mass were performed following the procedure reported in the instruction manual of equipment [28] and used in the past in our laboratory [29, 30] using as standard materials: indium (NIST SRM 2232), tin (NIST SRM 2220) and zinc (NIST SRM 2221a) for temperature; indium (NIST SRM 2232) for heat flow and a set of exactly weighed samples supplied by Shimadzu for mass. All calibrations of equipment were repeated every 2 weeks.

Scannings were carried out in the temperature range from 35 to 800 °C, at the heating rate of 10 °C min^{-1}, under flowing nitrogen (0.02 L min^{-1}) and in a static air atmosphere. Samples of about 5×10^{-3} g, placed in a 40-μL platinum open pan, were used for experiments. For TG analysis, the sample weight as a function of temperature was monitored and recorded by a PC connected with the DTG-60 apparatus. At the end of each run, the experimental data were used to plot the percentage of undegraded sample $(1 - D)\%$ as a function of temperature, where $D = (W_o - W)/W_o$, and W_o and W were the masses of sample at the starting point and during scanning. For DTA analysis, the heat flow of sample was monitored and recorded by the PC connected with the DTG-60 apparatus, in order to evaluate enthalpy and temperature of the observed phase transitions. The experiments were

Table 1 Structures of diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of bisphenol F (DGEBF), triglycidyl *p*-aminophenol (TGAP), 1,5-naphthalenediamine (ND) and 40:60 poly(ether-sulphone)–poly(etherether-sulphone) (PES–PEES)



Diglycidyl ether of bisphenol A

Diglycidyl ether of bisphenol F

Triglycidil *p*–aminophenol

1,5–Naphthalenediamine

40:60 PES–PEES

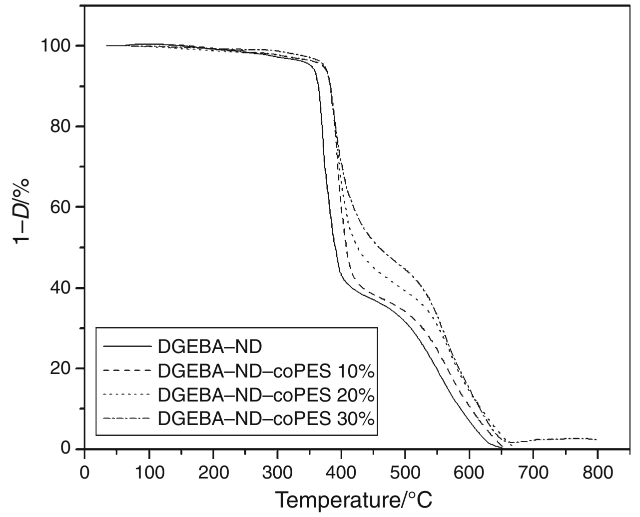


Fig. 1 TG curves in static air atmosphere of DGEBA–ND resin and DGEBA–ND–coPES resins

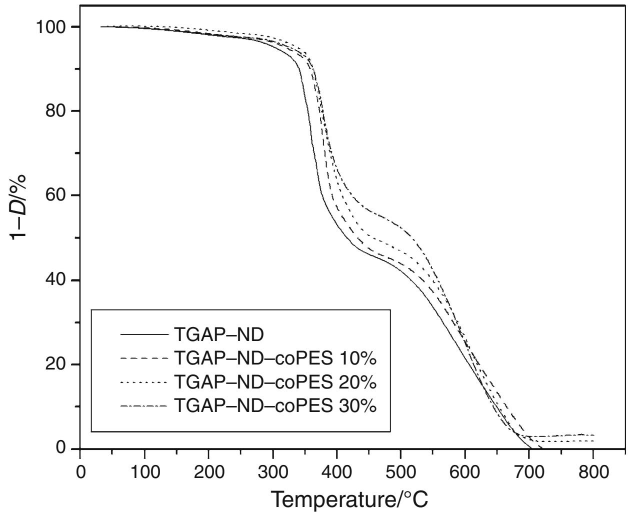


Fig. 2 TG curves in static air atmosphere of TGAP–ND resin and TGAP–ND–coPES resins

performed in triplicate and the considered values were averaged from those of three runs, the maximum difference between the average and the experimental values being within ±1 °C.

Results and discussion

The thermal behaviour of our compounds was studied by TG and DTA experiments in the temperature range

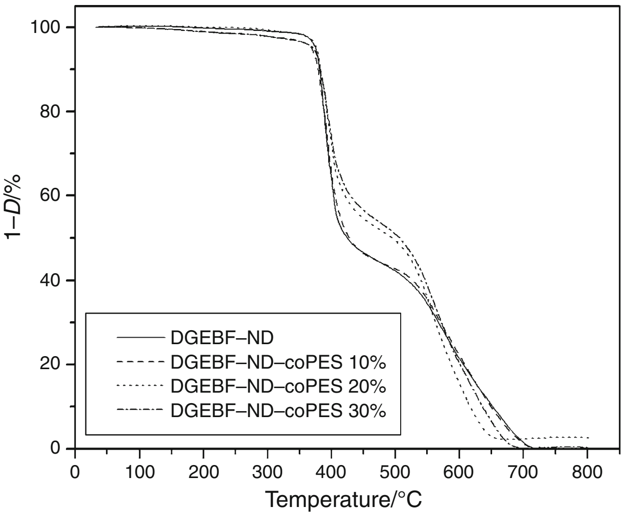


Fig. 3 TG curves in static air atmosphere of DGEBF–ND resin and DGEBF–ND–coPES resins

35–800 °C, in both flowing nitrogen and static air atmosphere, and the TG curves showed differences in the investigated environments.

The TG curves in oxidative atmosphere (Figs. 1, 2, 3) did not show any mass loss up to 200 °C, after which epoxy resin lost mass in two degradation steps. For all studied compounds were observed a first degradation stage, in every case included in the 350–450 °C temperature range, associated with the most part of mass loss (60–65%), immediately followed by another one at higher temperature without char formation (Table 2).

By contrast, the TG curves in inert atmosphere (Figs. 4, 5, 6) evidenced a single step of degradation for all compounds, with an overall mass loss, after the complete temperature scan, ranging from 85 to 69%. From the data in Table 2, in which residue % together with initial decomposition temperature and temperature at maximum degradation rate are reported, is possible to note that the amount of residue does not seem to be influenced by the percentage of toughener.

The temperatures of DTG peaks (T_m), which are the temperatures at maximum mass loss rate, as well as the T_i values, indicate that the degradation process starts at the same temperature range independently of the used atmosphere (Table 2).

The initial temperatures of decomposition, which are a measure of thermal stability and can be obtained by the experimental curves as the intersection between the starting mass line and the maximum gradient tangent to the TG curve, were determined and used for the comparisons among the various compounds investigated.

The DTA analyses confirmed the different behaviour of our compounds in the experimental atmospheres used.

A sharp exothermic DTA peak, followed, by another broad exothermic one at higher temperature, was obtained, for all investigated compounds in static air atmosphere (Figs. 7, 8, 9). By contrast, under nitrogen, all studied epoxy resins exhibited a single sharp exothermic DTA peak (Figs. 10, 11, 12). The temperatures of the main DTA peaks (T_p), as well as exothermic enthalpy values associated and glass transition temperatures, of various compounds in both studied environments are reported in Table 3.

The overall picture of the results from thermal experiments suggests some considerations:

Table 2 Initial decomposition temperatures (T_i), temperatures at maximum rate of mass loss (T_m) for the main degradation stage and residue % of the studied epoxy resins in flowing nitrogen and in static air atmosphere

Compounds	Nitrogen flow			Air static atmosphere		
	T_i/°C	T_m/°C	Residue/%	T_i/°C	T_m/°C	Residue/%
DGEBA–ND	374.6	385.9	17.0	374.1	384.8	0
DGEBA–ND–coPES 10%	376.9	387.2	14.7	378.8	386.1	0
DGEBA–ND–coPES 20%	378.2	390.4	14.7	382.7	388.8	0
DGEBA–ND–coPES 30%	380.3	392.2	19.6	382.6	391.5	1.5
TGAP–ND	355.8	370.3	25.6	357.3	376.1	0
TGAP–ND–coPES 10%	358.8	370.8	28.5	358.1	376.2	0
TGAP–ND–coPES 20%	360.3	374.0	30.7	362.7	376.9	0.8
TGAP–ND–coPES 30%	361.5	377.4	32.4	364.2	378.1	0.8
DGEBF–ND	373.8	385.9	19.9	376.8	386.6	0
DGEBF–ND–coPES 10%	373.8	385.9	23.6	376.8	389.2	0
DGEBF–ND–coPES 20%	377.3	390.6	23.4	377.3	398.5	2.4
DGEBF–ND–coPES 30%	376.0	391.0	23.4	379.1	402.0	0

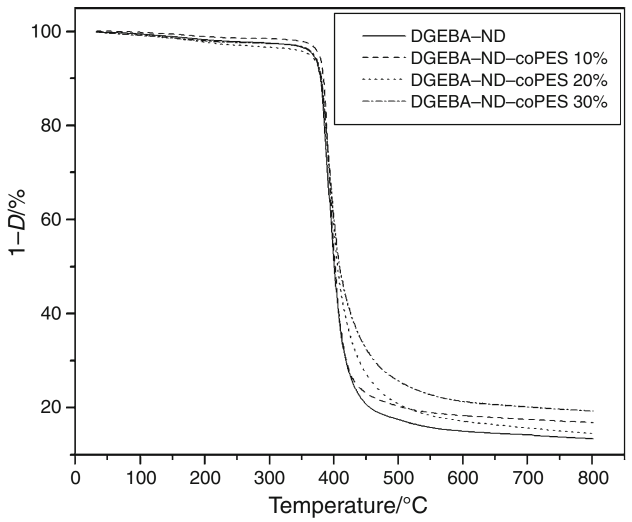


Fig. 4 TG curves under nitrogen flow of DGEBA–ND resin and DGEBA–ND–coPES resins

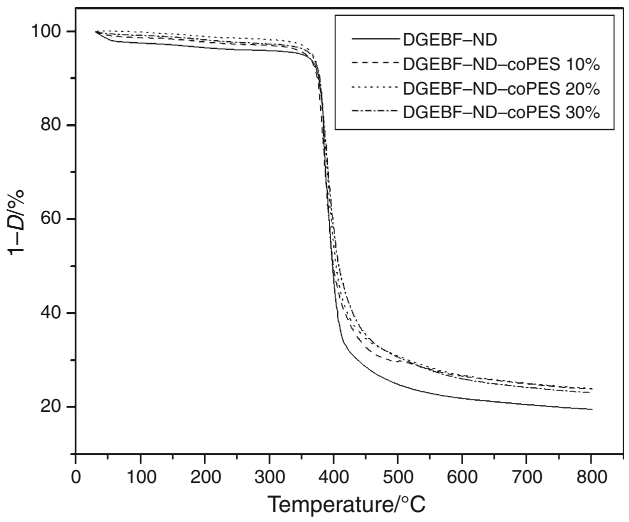


Fig. 6 TG curves under nitrogen flow of DGEBF–ND resin and DGEBF–ND–coPES resins

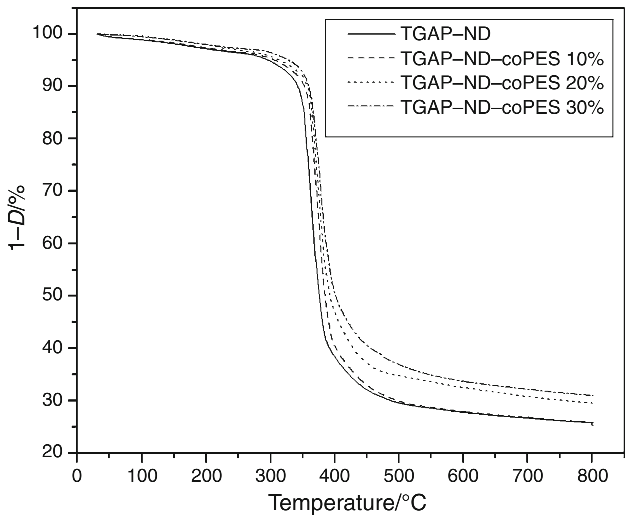


Fig. 5 TG curves under nitrogen flow of TGAP–ND resin and TGAP–ND–coPES resins

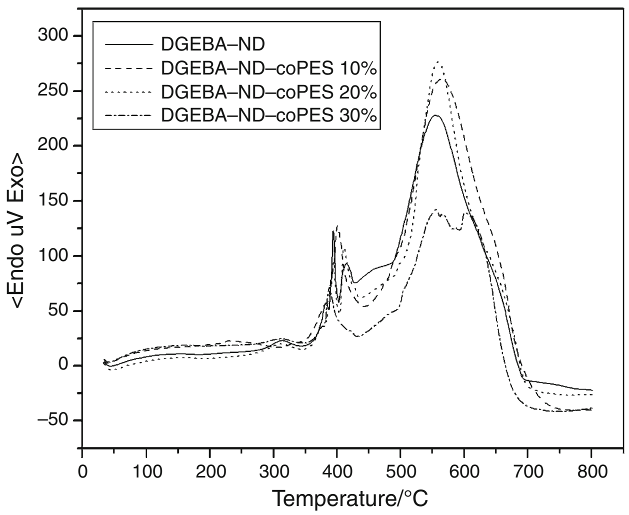


Fig. 7 DTA curves in static air atmosphere of DGEBA–ND resin and DGEBA–ND–coPES resins

- the TG curves and the related quantitative data of mass loss as well as the DTA curves clearly indicate that the degradation mechanism under nitrogen of the studied epoxy resins is different from that in air, where oxygen appears to play an active role in the decomposition process. The first DTA peak in both the studied environments might be due to the exothermic reaction caused by chain scission and resin decomposition, resulting in fragmentation of the resin into low molecular weight products [31]. The first stage lead to production of a carbonaceous residue, which is stable at lower temperatures, but is oxidised at higher temperature. The final exothermic reaction is mainly due to oxidation of this residue. This char oxidation stage in air (confirmed by the absence of the second DTA peak in the inert atmosphere) occurs in the temperature range 500–700 °C and causes about a 40% mass loss, whereas no mass loss is observed under nitrogen flow, leaving a higher char residue.
- the initial decomposition temperatures of our compounds in both studied environments, are higher [32] or, in some cases, of the same magnitude than similar compounds [33–35], thus indicating a good heat resistance. For all investigated epoxy resins the degradation in air started roughly at the same temperature than in flowing nitrogen showing that the beginning of

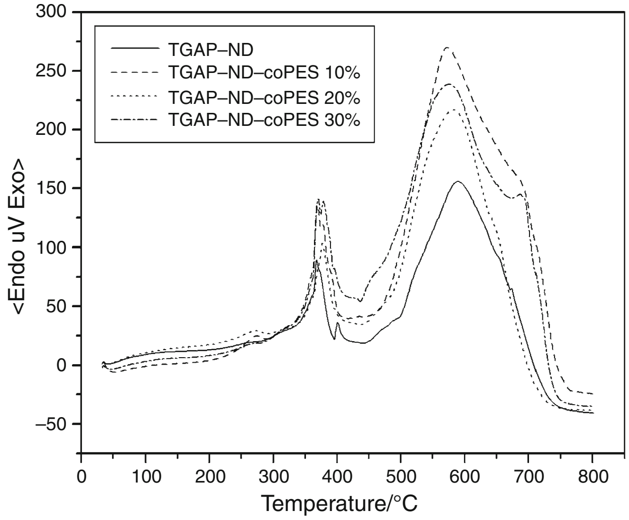


Fig. 8 DTA curves in static air atmosphere of TGAP–ND resin and TGAP–ND–coPES resins

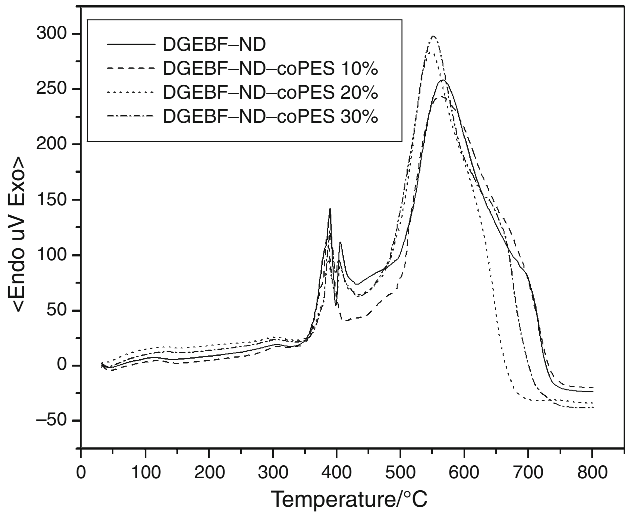


Fig. 9 DTA curves in static air atmosphere of DGEBF–ND resin and DGEBF–ND–coPES resins

the degradation process is not affected by the used atmosphere.

- the introduction of various percentage of toughener into the epoxy resin does not lower the thermal stability, as evidenced by the found T_i and T_m values, in both studied environment (Table 2), that remain substantially constant with increasing the amount of copolymer, within the range we considered.

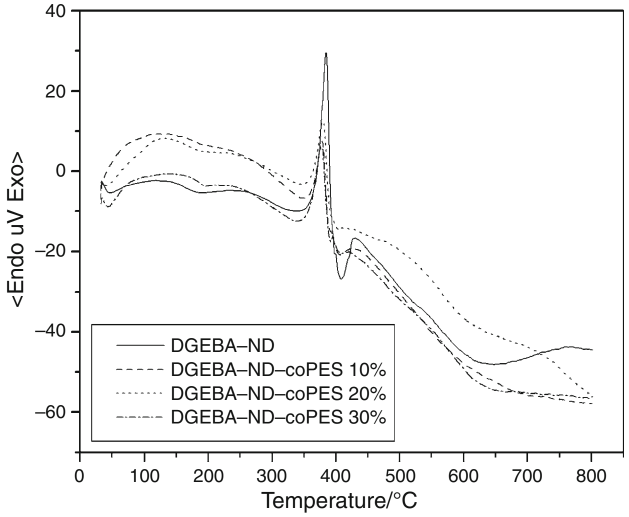


Fig. 10 DTA curves under nitrogen flow of DGEBA–ND resin and DGEBA–ND–coPES resins

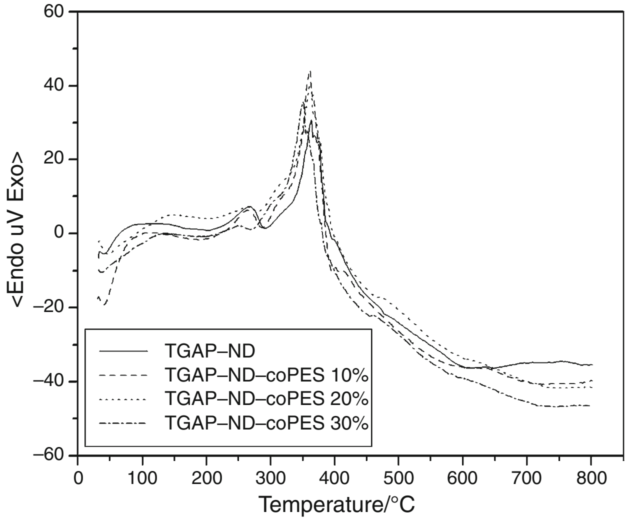


Fig. 11 DTA curves under nitrogen flow of TGAP–ND resin and TGAP–ND–coPES resins

Nevertheless, in our opinion, for the evaluation of the overall thermal stability of a compound we must take into account not only the heat resistance (which depends on the initial decomposition temperature), but, also, the degradation rate. This last parameter is more relevant when the initial decomposition temperatures of the compounds compared are close with each other [36]. Moreover, decomposition is a kinetic process thus the degradation rate is very important for applications because it characterise the speed of the process itself. This is the case of the resins here investigated. If we consider the data in Table 2, we observe that differences ($T_m - T_i$), which can be roughly considered a measure of the degradation rate, are similar in both atmospheres thus indicating the same degradation rates for all epoxy systems. These results suggest that the introduction of a variable percentage of toughener to the epoxy resins does not produce oxidation inhibition and more generally does not decrease their thermal stability.

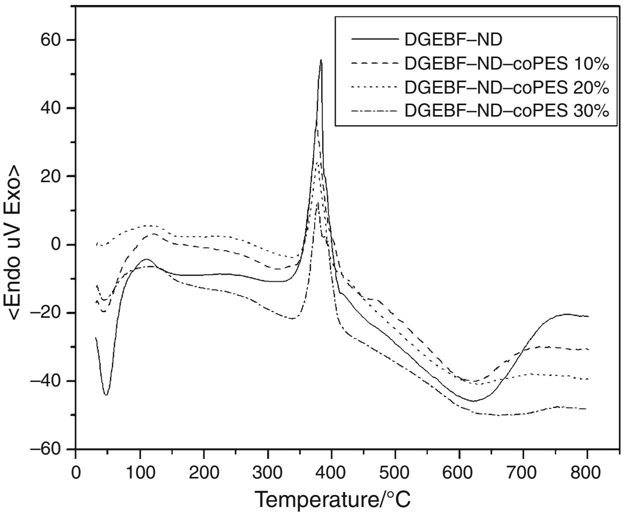


Fig. 12 DTA curves under nitrogen flow of DGEBF–ND resin and DGEBF–ND–coPES resins

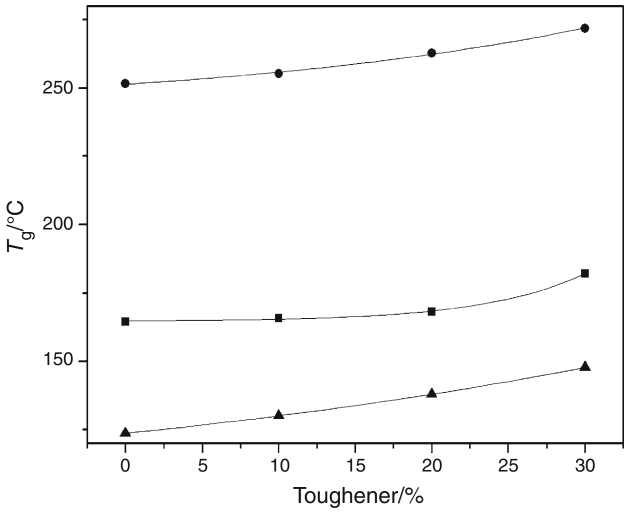


Fig. 13 Glass transition temperatures (T_g) as a function of coPES percentage

- even though the differences of T_i values among various compounds in oxidative experimental conditions as well as in inert atmosphere were not very large, they allowed us to make a heat resistance classification. On the basis of this classification the DGEBA–ND-toughened systems appear the most thermally stable, followed by the DGEBF–ND-toughened systems and then by the TGAP–ND-toughened systems.
- the temperatures of DTA peaks under nitrogen (Table 3) were close to those of corresponding DTG peaks (Table 2), thus suggesting that the exothermic effects measured are due to the decomposition process of compounds investigated. An analogous correspondence among the temperatures of first and the second exothermic DTA peaks and DTG peaks was found in static air atmosphere. The enthalpy values associated with DTA peaks are reported in Table 3 also.
- finally the glass transition temperatures of toughened epoxy resins are higher than that of epoxy resin, and increase with an exponential trend as a function of toughening degree (Fig. 13) thus indicating better thermal stability for toughened systems in service condition. From this point of view, the suitable epoxy system is the TGAP–ND.

Table 3 Temperature (T_p) and enthalpy ($-\Delta H$) of DTA peaks of the studied epoxy resins in flowing nitrogen and in static air atmosphere

Compounds	Nitrogen flow			Air static atmosphere			
	T_p/°C	$-\Delta H$/(J g^{-1})	T_g/°C	T_{p1}/°C	$-\Delta H$/(J g^{-1})	T_{p2}/°C	$-\Delta H$/(J g^{-1})
DGEBA–ND	375.3	498.49	164.5	387.8	874.09	554.4	15390
DGEBA–ND–coPES 10%	376.6	328.71	165.8	394.4	881.26	555.3	18180
DGEBA–ND–coPES 20%	378.0	337.97	168.3	395.2	935.50	559.8	15230
DGEBA–ND–coPES 30%	380.2	276.34	182.2	392.5	861.50	559.9	14870
TGAP–ND	362.8	1192.23	251.6	368.6	1320	581.93	16150
TGAP–ND–coPES 10%	361.6	1770.56	255.2	369.9	1450	573.0	22220
TGAP–ND–coPES 20%	362.8	1260.85	262.8	371.0	1490	589.7	21100
TGAP–ND–coPES 30%	363.6	1181.09	271.9	377.8	1712	576.1	24620
DGEBF–ND	378.1	942.95	123.6	388.0	884.98	567.8	14700
DGEBF–ND–coPES 10%	377.2	867.25	130.1	387.2	1150.07	562.7	18530
DGEBF–ND–coPES 20%	377.9	551.70	137.9	390.1	808.56	548.4	20258
DGEBF–ND–coPES 30%	383.5	587.90	147.8	389.5	1270.59	552.1	20781

Conclusions

This work is the final part of a wider research concerning the toughening of epoxy resins with thermoplastics. In this article, some epoxy resins toughened by amino-ended PES–PEES copolymer, were characterised and their degradation, in flowing nitrogen and in static air atmosphere, was followed by both TG and DTA techniques. The results have been encouraging because the glass transition temperature increases with the toughener percentage and all compounds showed high thermal stability, thus suggesting the possibility of their use also in quite drastic conditions.

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