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Curing kinetics and thermomechanical properties of latent epoxy/carbon fiber composites

S Dalle Vacche, V Michaud, M Demierre, P-E Bourban and J-A E Månson
Laboratoire de Technologie des Composites et Polymères, Ecole Polytechnique Fédérale de Lausanne, Station 12, CH-1015 Lausanne, Switzerland

e-mail : sara.dallevacche@epfl.ch

Abstract. In this work, resins based on diglycidyl ether of bisphenol A (DGEBA) epoxy and a latent hardener, dicyandiamide (DICY), as well as carbon fiber (CF) composites based on them, were prepared with three commercial accelerators: a methylene bis (phenyl dimethyl urea), a cycloaliphatic substituted urea, and a modified polyamine. The curing kinetics of the three DGEBA/DICY/accelerator systems were investigated by chemorheology and differential scanning calorimetry (DSC), in isothermal and over temperature change conditions. Differences in the reaction onset temperature, and in the glass transition temperature (T_g) were highlighted. For curing of thick resin samples, a slow curing cycle at the lowest possible temperature was used, followed by high temperature (160 – 180 °C) post-curing. Indeed, fast curing at higher temperatures caused the formation of hot spots and led to local burning of the samples. The obtained thermomechanical properties, assessed by ultimate tensile testing and dynamic mechanical analysis (DMA) in single cantilever configuration, were all in the expected range for epoxy resins, with tensile moduli close to 3 GPa and $T_g > 140$ °C. The long-term stability of these resins at room temperature was verified by DSC. Composite samples were prepared by hand lay-up by manually impregnating four layers of 5-harness satin CF textile, and curing in vacuum bag. Impregnation quality and void content were assessed by optical microscopy. The flexural properties of the post-cured composites were assessed by three-point bending test at room temperature and showed no relevant differences, all composites having bending moduli of 45 - 50 GPa. Finally, composites cured with a faster high temperature curing cycle (20 min at 140 °C) were prepared with the DGEBA/DICY/ methylene bis (phenyl dimethyl urea) system, obtaining similar properties as with the slower curing cycle, showing that the prepreg system allowed more flexibility in terms of curing cycle than the bulk resin samples.

1. Introduction

Epoxy/carbon fiber prepregs are used in a wide range of applications, including e.g aerospace, boat building, and automotive. Due to their reactivity at room temperature, commonly used epoxy prepregs need to be stored at -18 °C and usually have a short "out-life". For application such as on site repair, where cold storage is not practical, the use of dry fibers and two-component epoxy resins, which are mixed at the time of use, is preferred. Latent curing systems based on dicyandiamide (DICY) are only reactive above a certain temperature; nevertheless this comes at the expense of a high curing temperature (> 180 °C) and time [1 - 3]. Several types of accelerators, which enhance the reactivity of the resin, still guaranteeing a certain extent of room temperature stability, have been developed and studied [4, 5]. The use of an epoxy/DICY based resin as a matrix for carbon fiber prepregs would allow their long-term storage at room temperature, reducing storage costs and simplifying logistics.

However prepregs based on such systems, and related literature, are still not widely available. Some studies recently appeared on glass and carbon fiber prepregs, either house made or commercial [6 - 9]. This work investigates the possibility of producing out of autoclave carbon fiber composites based on epoxy/DICY latent resin formulations containing different commercial accelerators, comparing their room temperature stability and properties of the cured material.

2. Experimental

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin with EEW = 184-190 (Epikote™ Resin 828 by Momentive Performance Materials Inc., Waterford, NY, USA) was used, in combination with different latent hardener/accelerator systems. Two similar grades of the latent hardener, dicyandiamide (DICY), were obtained from two suppliers: Omicure™ DDA 10 by CVC Thermoset Specialties (Moorestown, NJ, USA), mean particle size 12 μm, and Amicure® CG1200G by Air Products Nederlands B.V. (Utrecht, The Netherlands), particle size 11 μm. Two accelerators were used in combination with DDA10, namely Omicure™ U-52M, a methylene bis(phenyl dimethyl urea), and Omicure™ U-35M, a cycloaliphatic substituted urea, both by CVC Thermoset Specialties (Moorestown, NJ, USA). Ancamine® 2441 (Air Products Nederlands B.V., Utrecht, The Netherlands), a modified polyamine that can be used both as hardener and as accelerator for DICY, was used in combination with Amicure® CG1200G.

Table 1. Compositions (phr) of the epoxy resin formulations used in this study, with the corresponding time to double viscosity (t_{shelf}) and glass transition temperatures of the cured resins (T_g) determined on DSC second scan, (* first DSC scan to 275°C at 20°C per minute, **first DSC scan at 10 °C/min) reported by the suppliers).

Code	Epikote 828	Omicure DDA 10	Amicure CG1200G	Omicure U-52M	Omicure U-35M	Ancamine 2441	t_{shelf} (weeks)	T_g (°C)
ED_U52	100	8	-	1	-	-	57	133*
ED_U35	100	8	-	-	1	-	> 70	129*
EA_A	100	-	6	-	-	5	> 12	135**

In order to prepare the resin formulations, the DGEBA epoxy resin was heated to 40 °C to decrease viscosity and the hardener and accelerator were mixed into it with a mechanical stirrer for 15 min. The mixture was then degassed in a vacuum oven at 40 °C prior to use. The compositions were chosen according to the indications in the datasheets, and are summarized in Table 1, together with their shelf lives (t_{shelf}) at room temperature and the glass transition temperatures (T_g) of the cured resins indicated by the suppliers.

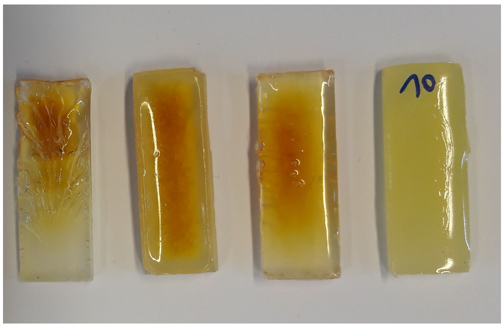

Figure 1. Three resin samples (left side) cured at high temperature, showing local burning, and one sample (last on the right) cured at low temperature.

Resin plates with a thickness of 3 - 4 mm for dynamic mechanical analysis and tensile tests were cured in open silicon molds. As preliminary curing tests at temperatures above 135 °C led to inhomogeneous curing or local burning (Figure 1), the samples were initially slowly cured at low temperature until solid, then the temperature was increased to 160 °C during 20 min. Finally they were demolded, and part of them were post-cured for 10 min at 180 °C. The temperature and duration of the initial curing were adapted according to the resin formulation, as summarized in Table 2.

In order to fabricate composite plates, four layers of 5-harness satin carbon fiber fabric were weighed and then impregnated by hand with the resin formulations. The four superposed layers of impregnated fabric were then sealed in a vacuum bag, which was placed either in an oven or in an autoclave. Vacuum was applied at room temperature for 1 hour for debulking, and then the selected curing cycle was carried out. After demolding, the composite was weighed and the mass of resin was determined by subtracting the mass of the fibers. From the mass of the fibers and resin, and their densities, the volume fraction of fibers (on a void free basis) was calculated to be $V_f = 0.52 \pm 0.02$. Specimens were then cut with a diamond saw and post-cured. Curing and post-curing cycles are detailed in Table 3.

Table 2. Cured and post-cured resin samples

Code	Resin formulation	Cure cycle	Post-cure cycle
ED-U52-C	EDU52	60 min at 100 °C 30 min at 115°C 20 min at 160 °C	no
EDU52-PC			10 min at 180 °C
ED-U35-C	EDU35	30 min at 115 °C 30 min at 120 °C 50 min at 125 °C 20 min at 160 °C	no
ED-U35-PC			10 min at 180 °C
EA-A-C	EAA	60 min at 100 °C 20 min at 160 °C	no
EA-A-PC			10 min at 180 °C

Table 3. Carbon fiber composite samples

Code	Resin formulation	Cure cycle	Post-cure cycle
ED-U52_F	ED-U52	60 min @ 120 °C	20 min @ 160 °C + 10 min ramp to 180 °C + 10 min @ 180 °C
ED-U52_F_140	ED-U52	20 min @ 140 °C	
ED-U52_F_140_A	ED-U52	20 min @ 140 °C in autoclave (P = 0.5 MPa)	
ED-U35_F	ED-U35	60 min @ 120 °C	
EA-A_F	EA-A	60 min @ 120 °C	

Differential scanning calorimetry was performed with a Q100 DSC (TA Instruments, USA) under a constant N_2 flow of 50 mL/min. Non-isothermal scans on fresh and aged uncured resin consisted of a heating cycle from 40 °C and 250 °C at 10 °C min^{-1}. Isothermal scans on uncured resins were performed by rapidly equilibrating to the desired temperature, and holding the temperature for a fixed time. After each non-isothermal or isothermal scan the sample was left in the DSC cell where it was rapidly equilibrated to -40 °C, and a heating cycle was performed up to 250 °C at 10 °C min^{-1} to assess the glass transition temperature and the residual reactivity.

Chemorheology was performed with an AR2000 rheometer (TA Instruments, USA), in oscillatory mode, holding at 25 °C for 10 min, then increasing temperature from 25 °C to 180 °C at 10 °C min^{-1} and finally holding at 180 °C until the complex viscosity reached a plateau. The frequency was 1Hz and the strain was controlled between 0.01% and 20% in order to follow the viscosity evolution.

Dynamic mechanical analysis (Q800 DMA, TA Instruments, USA) was performed in single cantilever (resin specimens) or in three-point bending (composite specimens) configurations, with an excitation frequency of 1 Hz. The temperature was raised from 25 °C to 240 °C at a heating rate of

3 °C min^{-1}. For single cantilever test the applied amplitude was 15 μm, while for 3-point bending a strain of 0.05 % was applied.

The mechanical properties in tension (resin specimens) and three-point bending (composite specimens) were assessed at room temperature with a Universal Testing Machine (UTM, LFM-125kN, Walter & Bai) equipped with a 1kN load cell (HBM Test and Measurement, Darmstadt, Germany). The tensile measurements were carried out on dog-bone shaped specimens at a speed of 1.2 mm min^{-1}, while for 3-point bending the speed was set at 6 mm min^{-1} and the span at 40 mm.

Optical micrographs were taken with an Olympus BX60 microscope equipped with a camera. The samples were embedded in clear epoxy resin and wet ground with SiC paper down to 4000 grit. Porosity was estimated from the micrographs by image analysis with ImageJ software.

3. Results and discussion

3.1. Curing kinetics and aging

The DSC temperature ramps performed on fresh uncured resin formulations revealed different curing kinetics depending on the hardener/accelerator system, as shown in Figure 1. ED-U52 showed an onset temperature of 130 °C and ED-U35 of 140 °C. Both exhibited a relatively narrow exotherm peak, with maxima at 158 °C and 166 °C, and reaction enthalpies equal to 375 ± 52 J/g and 352 ± 52 J/g, respectively. No residual reactivity appeared above 190 °C. EA-A showed a broader exotherm peak, with an onset of reaction already at 65 °C and a peak maximum at 145 °C. A second small peak with a maximum at 214 °C, close to the melting temperature of DICY, seems to indicate that some residual reaction occurred after melting of undissolved DICY. The reaction enthalpy was 346 ± 19 J/g. ED-U52 and ED-U35 were tested after aging at room temperature for 8 months. Their reaction enthalpy and their T_g were not significantly different from those measured on fresh resins, however aged ED-U52 reacted at slightly lower temperature than the fresh one, with an onset of reaction at 125 °C and a peak maximum at 152 °C. On the other hand, although the reaction enthalpy of EA-A after 6 months aging was not found to have dramatically decreased (324 J/g), and the obtained T_g was equal to that of the fresh resin, after 8 months the resin had become a hard and brittle reticulated solid, and DSC was not carried out on it. ED resins thus seem better adapted as the resin of a room-temperature storage prepreg, as already indicated from Table 1 for the pure resin.

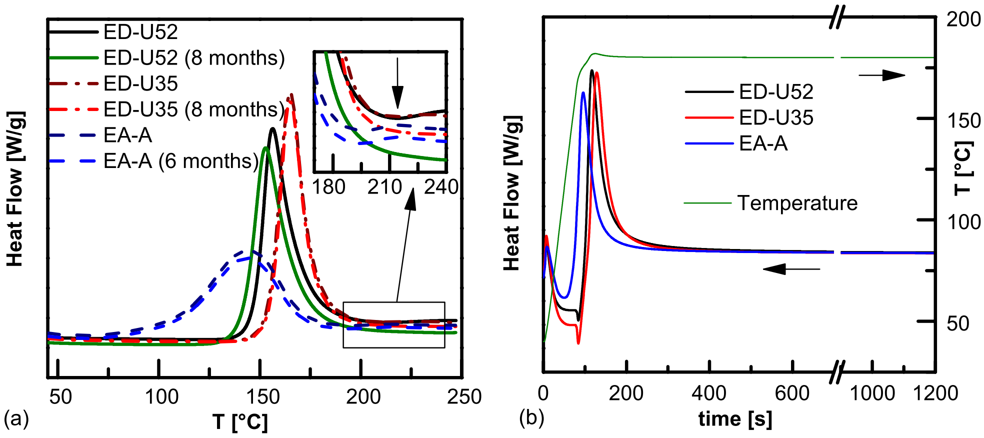

Figure 2. (a) Non-isothermal DSC scans of fresh and aged uncured resins, the inset highlights the reaction peak at 214 °C for EA-A resins, and (b) heat flow as a function of time during isothermal curing of fresh resins at 180 °C.

Isothermal curing at 180 °C during 20 min (Figure 2b) led to fully cured resins for all the three accelerated formulations, as demonstrated by the absence of residual reactivity during the second DSC scan. Increasing the curing time up to 1 h did not further increase T_g, which was 141 °C for ED-U52, 137 °C for ED-U35 and 138 °C for EA-A. As shown in Figure 2b, EA-A started reacting well before the DSC cell could reach the isothermal temperature, considerably faster than ED-U52 and ED-U35. The reaction of ED-U52 was only somewhat more rapid than that of ED-U35, as shown by the maximum of the reaction peak being delayed of about 10 s for the latter.

The complex viscosity at 25 °C was found to be similar for the three accelerated formulations, i.e 15 Pa s for ED-U52 and ED-U35, and 18 Pa s for EA-A. The viscosity initially decreased with increasing temperature, and then increased due to the curing reaction (Figure 3). The chemorheology test confirmed the DSC results. Preliminary tests performed on resin/hardener mixtures, with no accelerators, had shown that, with DICY alone, the viscosity increase started only after about 1 – 2 min at 180 °C. All accelerated formulations, ED-U52, ED-U35, and EA-A, showed a faster viscosity build-up than with DICY alone. The viscosity of ED-U52 started to increase at a lower temperature and more rapidly than that of ED-U35, while the plateau value was similar for the two systems. For EA-A, the viscosity increase started already at 130 °C and proceeded very rapidly to reach already at 160 °C a viscosity close to that of the plateau value of the other two resins, However for this resin the instrument was not able to follow the viscosity evolution up to 180 °C and a plateau value at this temperature could not be attained to compare with the other resins.

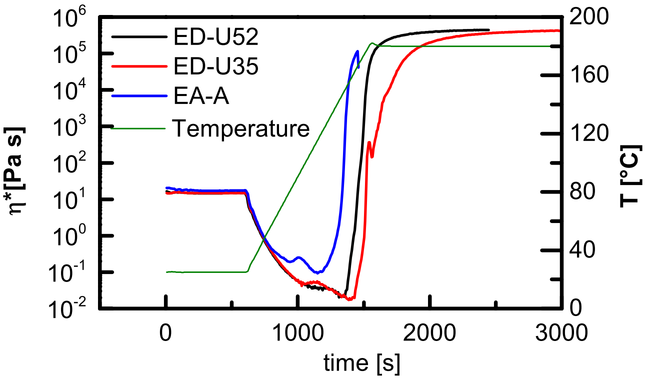

Figure 3. Complex viscosity η* of fresh resins and temperature during cure in the rheometer.

3.2. Properties of cured resin

Despite attempting to optimize the slow cure cycle for ED-U35 formulation, it was not possible to avoid a certain degree of settling of the hardener and accelerator, and the specimens showed a slight cure gradient through the thickness. This phenomenon was not observed for the other two resins, possibly due to the faster viscosity increase that hindered the settling of hardener/accelerator particles.

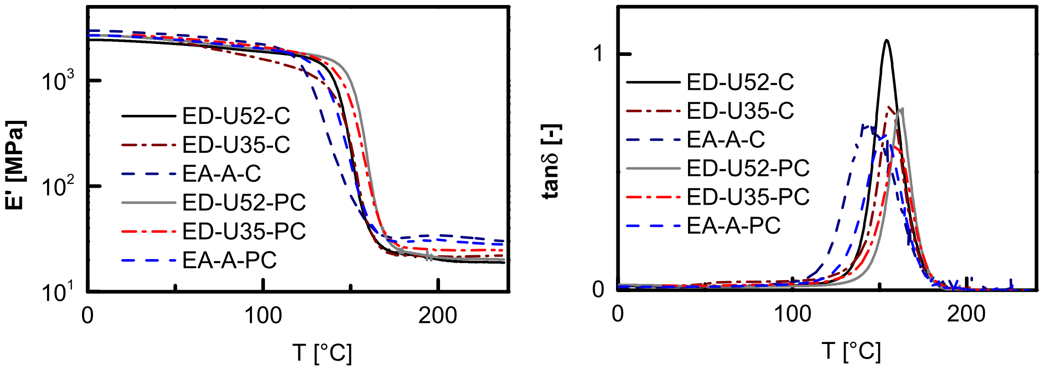

Figure 4. Storage modulus and tanδ of cured and post-cured resin specimens

The cured resins ED-U52-C, ED-U35-C and EA-A-C, although having similar properties at room temperature, exhibited a different evolution of E’ and tanδ with temperature (Figure 4). ED-U52-C showed the highest T_g, with a narrow tanδ peak centered around 154 °C. ED-U35-C on the other hand, showed a slight drop of the storage modulus and a shoulder on the tanδ curve above 40 °C, followed by a steeper E’ drop and a narrow tanδ peak at 156 °C. Finally EA-A-C had a wide glass transition region, indicated by a broad tanδ peak, at 145°C. All the three cured resins exhibited some degree of residual reactivity after T_g, as indicated by a very slight increase of their storage moduli around 180 – 200 °C. ED-U52-PC and ED-U35-PC had similar storage moduli over the entire range of temperatures, and a narrow tanδ peak centered around a T_g of 160 °C. On the other hand EA-A-PC had similar storage modulus as the other post-cured resins before and after the glass transition region, however the glass transition occurred at somewhat lower temperature (145 °C) with a wider tanδ peak. The storage moduli at room temperature were similar for all cured and post-cured resins, and were in the range of 2.5 ± 0.3 GPa.

The tensile moduli of post-cured specimens of all the three investigated resin formulations did not show statistically significant differences, with values in the 2.6 – 3.1 GPa range, as shown in Figure 5. ED-U52-PC and ED-U35-PC specimens had similar values of stress and strain at break, close to 60 MPa and just above 3.5 %, respectively. All the values obtained for the tensile properties fall in the typical range for a DGEBA epoxy.

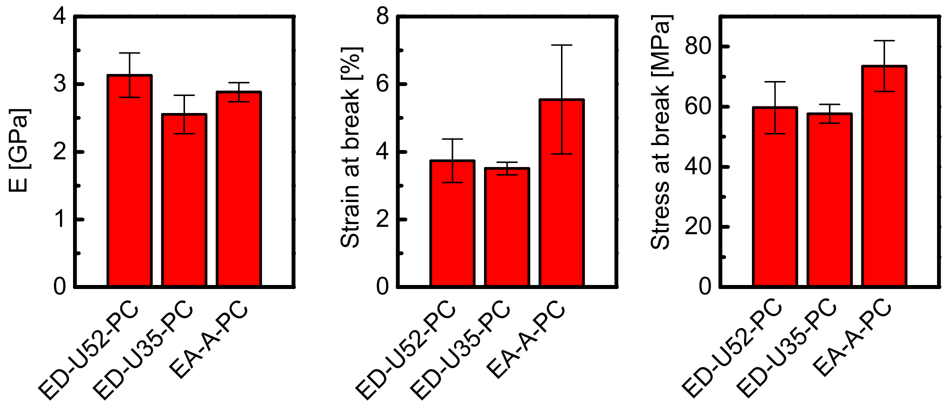

Figure 5. Tensile properties of post-cured resins

3.3. Properties of carbon fiber composites

Optical micrographs of cross-sections of composite specimens are given in Figure 6. The composites ED-U52-F, ED-U35-F and EA-A-F, which went through the same curing cycle, and ED-U52-F-140, which was cured at higher temperature and shorter time than his homologous ED-U52-F (see Table 3), showed similar impregnation and a porosity of about 6 %. The voids were located mostly at the interface between fabric layers. On the other hand ED-U52-F-140-A, for which the curing cycle, with the same temperature and time than ED-U52-F-140, was carried out in an autoclave, had lower porosity, i.e. about 4 %. These values are rather high even for a hand lay-up composite, but could be attributed to the high viscosity of the DGEBA resin, combined with insufficient degassing steps.

The storage moduli (Figure 7) of the composite specimens ED-U52-F, ED-U35-F and EA-A-F had very similar values at temperatures below 100 °C, which was to be expected on the basis of similar matrix properties, fiber volume fraction, and porosity. Finally, comparing ED-U52-F-140 with ED-U52-F-140-A, a difference in the E’ before glass transition was observed, that can be attributed to the lower porosity obtained with autoclave curing. On the other hand, glass transition occurred at similar temperature for all the specimens, as shown by the similar tanδ plots (Figure 7).

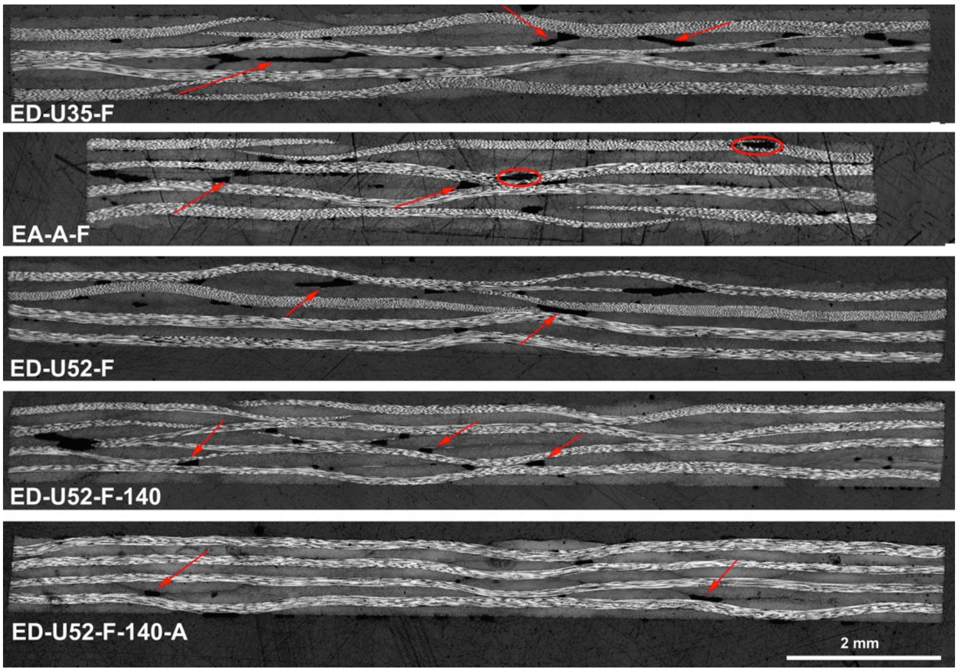

Figure 6. Optical micrographs of cross-sections of carbon fiber composites. Examples of voids at the interfaces between CF layers are indicated by arrows, and voids inside the layers by ellipses.

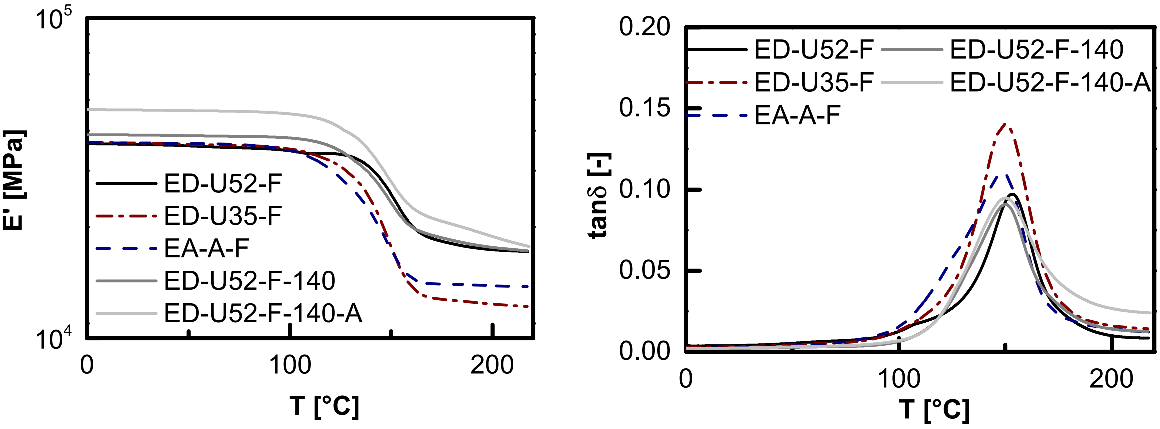

Figure 7. Storage moduli and tanδ as a function of temperature for composite specimens

The flexural properties of vacuum bag cured composites (Figure 8) did not show relevant differences due to the type of hardener/accelerator system, or to the curing cycle, with the only exception of the lower flexural strength and marginally lower strain at break showed by EA-A-F specimens. An upper limit for the modulus of a composite containing a volume fraction V_f of carbon fibers in a 5-harness satin configuration may be estimated by the rule of mixtures $E_{long} = V_f \cdot E_f + (1 - V_f) \cdot E_m$. Introducing the values of the tensile moduli of the fibers and of the matrix (assumed to be E_f = 230 GPa and E_m = 3 GPa), and considering as a first approximation that half of the fibers contribute to the longitudinal modulus in a 5-harness satin fabric, a value of E_{long} of about 60 GPa is obtained. The flexural moduli obtained experimentally are thus not far from the theoretical upper value of the longitudinal modulus, considering the fiber crimp of the satin fabric, and the shear contribution to the flexural modulus value.

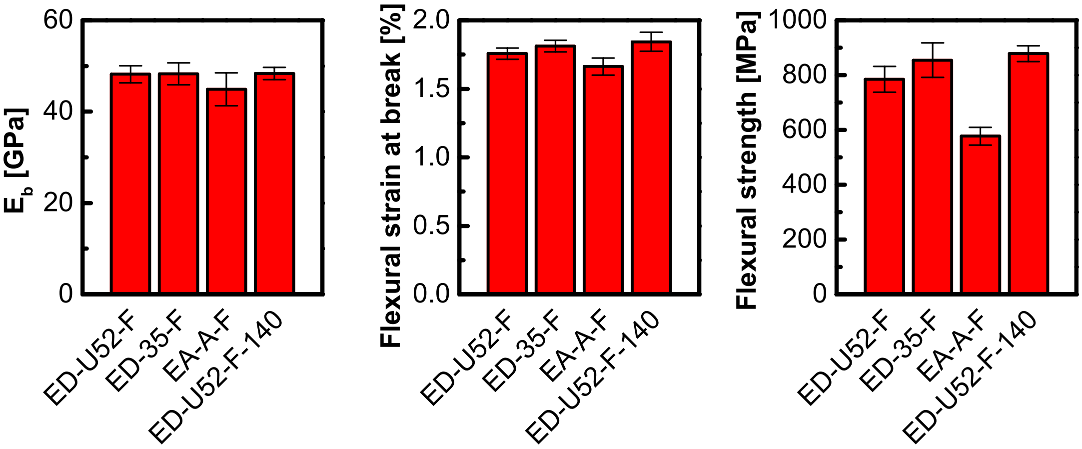

Figure 8. Flexural modulus (E_b), flexural strain at break and flexural strength of post-cured composites.

4. Conclusions

Among the three epoxy/DICY/accelerator systems considered in this work, ED-U52 and ED-U35 demonstrated no significant aging after 8 months storage of the resin at room temperature. EA-A, although still having retained a substantial degree of reactivity after 6 months, was found to have reticulated after 8 months, confirming its lower storage stability at room temperature. Nevertheless, when fully cured, both the bulk resin and the composite samples obtained from the three different accelerated resin formulations showed similar thermomechanical properties. Furthermore, when the resin systems were used as a matrix for carbon fiber composites it was demonstrated that the impregnation and the void content of the composite specimens cured in a vacuum bag were similar for all resin formulations, as expected on the basis of their similar viscosity at room temperature, resulting in similar mechanical properties. The void content decreased, and the storage modulus increased, as expected, when cure was performed in an autoclave.

This study indicated that vacuum bag curing of carbon fiber composites based on all the epoxy/DICY/accelerator systems considered is possible and leads to acceptable thermomechanical properties, although it would be desirable to decrease the void content, by e.g. using an epoxy resin with lower viscosity. Furthermore the three formulations led to similar properties of the composite specimens, and therefore the choice of a specific accelerator can be based on other considerations, as e.g. shelf life, desired curing temperature and time, or cost. These types of resin formulations could therefore be of interest for on site repair application that could not afford refrigerated storage of prepregs or the use of an autoclave.

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